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# ICE-MAKING MACHINES:

THE THEORY OF THE ACTION OF THE VARIOUS FORMS OF COLD-PRODUCING OR SO-CALLED ICE MACHINES  
(MACHINES A FROID).

TRANSLATED FROM THE FRENCH OF

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*Ingenieur des Mines.*

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## PREFACE.

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THE theory of Ice-Making Machines has assumed a new importance, since it has been shown that they may be worked to an economical advantage in some sections, even where natural ice is not difficult to be obtained.

But aside from any question of competition with natural ice in temperate climates, the subject is of great interest to those who find it desirable to produce and maintain a low temperature in places where the requisite quantity of ice would be too cumbersome, and where a refrigerating machine and its driving power can be easily accommodated. Such an example is afforded by the hold of a vessel sailing in a warm climate.

The conditions of effective working of the three classes of machines are clearly set forth in this little treatise.

G. W. P.



# ICE-MAKING MACHINES.

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## CHAPTER I.

§ 1. It has long been known that air is heated or cooled when compressed or dilated.

The mechanical theory of heat defines the conditions under which this heating or cooling is effected, and shows that these effects are proportioned to the external work performed by the air, with the restriction that in expanding the resistance overcome by the gas is always equal to the elastic force of the latter.

If  $t$  and  $t'$  represent successive temperatures of a unit weight of a permanent gas, which has been compressed or dilated under conditions above stated in producing an amount of work (either resistant or motive) equal to  $W$ , we shall have

$$t - t' = \frac{A}{c} W$$

A being the reciprocal of the mechanical equivalent of heat  $= \frac{1}{424}$  and  $c$  being the specific heat of the gas at constant volume.

In a saturated vapor a part of the thermal equivalent of the external work is transformed into latent heat; the other part alone becomes sensible under the form of external heat.

This is expressed in the fundamental equation

$$c_1(t-t') + (x\rho - x'\rho') = AW$$

in which  $c_1$  is the specific heat of the liquid,  $x$  the proportion of vapor in the unit of weight of mixture of liquid and vapor,  $\rho$  the latent heat of the vapor and  $W$  the external work accomplished.

We see from these equations that for the same quantity of heat transformed into work, the range of temperatures must be greater with a gas than with saturated vapors.

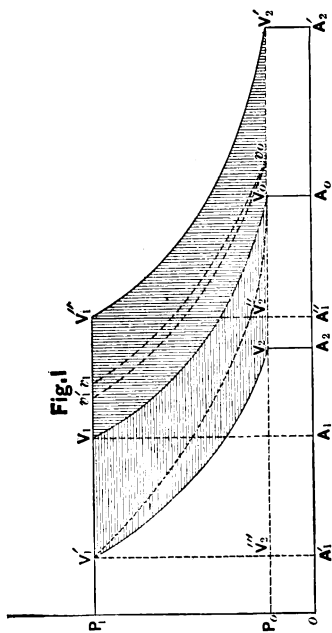
§ 2. Whether we employ a permanent gas or a vapor, the apparatus designed for the refrigerating effects is based upon the following series of operations:



Compress the gas or vapor by means of some external force, then relieve it of its heat so as to diminish its volume; next, cause this compressed gas or vapor to expand so as to produce mechanical work and thus lower its temperature. The absorption of heat at this stage by the gas, in resuming its original condition, constitutes the refrigerating effect of the apparatus.

When the cooling takes place at constant pressure, the cycle of operations can be represented by the diagram Fig. 1 in which the abscissas represent volumes, and the ordinates pressures.

The gaseous body taken at the pressure  $P_0$  and under the volume  $V_0$  is compressed to the tension  $P_1$  and the volume  $V_1$ . It is then cooled under constant pressure so that the volume  $V_1$  becomes  $V_1'$ , then it is allowed to expand, the pressure  $P_1$  becoming  $P_0$  and the volume changing from  $V_1'$  to  $V_2$ . Finally it is brought to the original volume  $V_0$  by transferring heat to it under constant pressure. The area  $V_0V_1V_1'V_2$  represents



the work expended and the line  $V_0V_2$ , the refrigerating effect obtained.

An inspection of the figure shows that a refrigerating machine is a heat engine reversed.

If instead of cooling the gas, to reduce it from the volume  $V_1$  to  $V_1'$ , it be heated so as to assume the volume  $V_1''$  greater than  $V_1$ , an amount of work is obtained which is represented by the vertically shaded area  $V_0V_2V_1''V_1$ ; the heat expended is represented by the length  $V_1V_1''$ .

It should be noticed that in the case of a permanent gas, the changes from volume  $V'$  to  $V_1'$  or  $V_1''$  and from  $V_2$  or  $V_2'$  to  $V_0$  are accompanied by corresponding changes in temperature. In the case of a condensable vapor these changes are effected at a constant temperature, the addition or subtraction of heat taking effect in an evaporation of the liquid or a condensation of the vapor.

§ 3. From this similarity between heat motors and freezing machines it results that all the equations deduced from the

mechanical theory of heat to determine the performance of the first apply equally to the second.

If  $Q_1$  be the quantity of heat taken from or added to a given mass, of compressed gas or vapor, and  $Q$  the quantity of heat necessary to subtract from or add to the expanded mass in order to bring it to its initial state,  $T_0$  and  $T_1$  the absolute temperatures corresponding to the volumes  $V_0$  and  $V_1$  and  $W$  the work, either active or resistant developed by the machine. The fundamental principle of the mechanical theory of heat, if the gas returns exactly to its primitive condition, affords the equation,

$$Q_1 - Q = AW$$

If the cycle of changes is the so-called cycle of Carnot; that is to say, if the lines  $V_1V_0$ ,  $V_1'V_2$ , and  $V_1''V_2'$  are adiabatic curves; then we have

$$\frac{Q}{T_0} = \frac{Q_1}{T_1} = \frac{Q_1 - Q}{T_1 - T_0}$$

The quantity of work developed by a heat motor, under these circumstances,

is for each heat unit or *calorie*, whatever the intermediate agent,

$$\frac{W}{Q_1} = \frac{1}{A} \cdot \frac{T_1 - T_0}{T_1}$$

✓ The efficiency depends upon the difference between the extremes of temperature.

✓ The performance of a refrigerating machine depends upon the ratio between the calories eliminated and the work expended in cooling.

✓ It is expressed by

$$\frac{Q}{W}$$

and we have

$$\frac{Q}{W} = \frac{AQ}{Q_1 - Q} = A \frac{T_0}{T_1 - T_0}.$$

This result is independent of the nature of the body employed.

✓ Unlike the heat motors, the freezing machines possess the greatest efficiency when the range of temperatures is small, and when the final temperature is elevated.

✓ In a freezing machine employing a va-

por,  $T_0$  being the absolute minimum final temperature, this final temperature  $T_2$  in a machine employing a permanent gas is different from the initial temperature  $T_0$ , and we have,

$$\frac{T_1}{T_0} = \frac{T_0}{T_2}$$

We can write for the efficiency

$$\frac{Q}{W} = A \frac{T_2}{T_0 - T_2}$$

Comparing the efficiencies of the two machines it is evident that the performance becomes less in proportion as we obtain lower final temperatures.

Theoretically there is no advantage in employing a gas rather than a vapor in order to produce cold even if the compression be made without addition or subtraction of heat.

The choice of the intermediate body would be determined by practical considerations based on the physical characteristics of the body, such as the greater or less facility for manipulating it; the extreme pressures required for the best effects, etc.

Air offers the double advantage that it is everywhere obtainable, and that we can vary at will the higher pressures independent of the temperature of the refrigerant. But it is cumbersome, and to produce a given useful effect the apparatus must be of large dimensions.

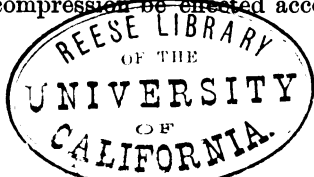
Liquids on the other hand allow the use of smaller machines, but are obtained only at a greater or less cost.

Furthermore the maximum pressure is determined beforehand by the temperature of the refrigerant, and depending on the nature of the volatile liquid; this pressure is often very high.

§ 4. The foregoing conclusions are based on the hypothesis that the compression and expansion follow the adiabatic lines  $V_0V_1$  and  $V_1'V_2$ , that is to say that the changes of volume and pressure follow the cycle of Carnot.

This hypothesis is realized when the cooling is accomplished outside of the compression cylinder and after the gas has been raised to the pressure  $P_1$ .

If the compression be effected accord-



ing to some cycle different from Carnot's, the efficiency, if it be a heat motor, would be diminished, but in a freezing machine it would be greater or less, depending upon the manner in which the successive operations were effected.

Suppose for example that instead of cooling, the gaseous body outside the compression cylinder, it be done during compression within the cylinder in such a manner as to maintain a constant temperature. This hypothesis would be graphically represented in Fig. 1 by replacing the adiabatic curve  $V_0V_1$  by the isothermic curve  $V_0V_1'$ . The work of resistance of the machine would then be represented by the curvilinear triangle  $V_0V_1V_1'V_2$ . The quantity of negative heat produced represented by the line  $V_0V_2$  remains the same. The efficiency of the freezing machine would be thus augmented as the resistant work of the motor would be less than the preceding case for the same quantity of negative heat produced.

The cooling of vapors during com-



pression is not readily realized, since it is effected at a constant temperature and one which is lower than the refrigerant. It is realized though somewhat incompletely in the case of permanent gases since their temperature during compression is above that of the refrigerant.

§ 5. The efficiency is calculated in the following manner.

We suppose the compression to be made at a constant temperature. Then by Marriotte's Law we have  $P_1 V_1 = P_0 V_0$ .

The work of resistance to compression would be

$$W_r = P_0 V_0 \cdot \ln \frac{V_0}{V_1} = RT_0 \ln \frac{V_0}{V_1}$$

and we shall have as in the preceding case.

$$AW_r = Q_1$$

R is a constant, uniform for the air at 29.27 inches and a unit of weight is supposed taken.

The gas dilating from the temperature  $T_0$  to  $T_1$  without gaining or losing heat, we shall have for the work of dilatation,

inclusive of the work at full pressure during introduction ;

$$AW_m = kc(T_0 - T_2) = Q.$$

The performance is represented by

$$A \frac{Q}{Q_1 - Q}$$

and we have

$$\begin{aligned} \frac{Q}{W_r - W_m} &= A \frac{Q}{Q_1 - Q} \\ &= \frac{kc(T_0 - T_2)}{RT_0 \ln \frac{P_1}{P_0} - \frac{kc}{A}(T_0 - T_2)}. \end{aligned}$$

We have also

$$\frac{c}{A} = \frac{R}{k-1};$$

$k$  is the ratio of specific heat at constant pressure to the specific heat at constant volume; this ratio is  $=1.41$  and is the same for all permanent gases.

It follows then

$$A \frac{Q}{Q_1 - Q} = A \frac{T_0 - T_2}{\left(\frac{k-1}{k}\right) T_0 \ln \frac{P_1}{P_0} - (T_0 - T_2)}$$

If the compression follows an adiabatic curve, we shall have for the efficiency—

calling  $T_1$  the absolute final temperature of the compression

$$A \frac{Q}{Q_1 - Q} = A \frac{T_0 - T_2}{T_1 - T_0 - (T_0 - T_2)^{\frac{k-1}{k}}}$$

and 
$$\frac{T_1}{T_0} = \left( \frac{P_1}{P_0} \right)^{\frac{k}{k-1}}$$

It is easy to show that

$$T_1 - T_0 \text{ or } T_0 \left\{ \left( \frac{P_1}{P_0} \right)^{\frac{k-1}{k}} - 1 \right\}$$

is greater than

$$\frac{k-1}{k} T_0 \log \frac{P_1}{P_0}$$

and consequently that the efficiency in the first case is less than in the second.

The employment of air presents a certain theoretical advantage over volatile liquids, inasmuch as it admits of cooling to a certain extent during compression.

We will now examine in succession some of the recently invented freezing machines (*machines à froid*). The Air Machine of M. Giffard; the Sulphurous Acid Machine of M. Pictet, and the Ammonia Machine of M. Carré.

## CHAPTER II.

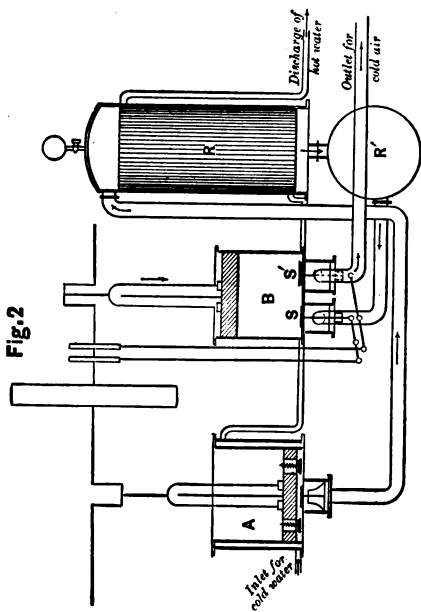
## GIFFARD'S AIR MACHINE.

§ 7. This machine consists of a single-acting cylinder A, the piston of which is furnished with two valves opening from without inward. This cylinder is surrounded with a jacket leaving a space within which circulates a current of cold water.

There is a second cylinder, B, also single-acting, and having a solid piston, and with a diameter a little smaller than the first. At the bottom of this cylinder are two openings closed by valves, opening, one outward and the other inward, and operated by levers which are worked by cams on the driving shaft.

The pistons are driven by crank connections with the main shaft.

The condenser R is a surface condenser and receives a current of cold water from the envelope of the compressor cylinder A. A Reservoir of wrought iron, R', is connected with the condenser by a tube and communicates also with the bottom of the expansion cylinder B.



§ 8. The air taken in at ordinary pressure is compressed in the cylinder A till it has the density of that in the reservoir; it is then allowed to flow into the condenser R and the reservoir R'. During this passage it loses a great part of the sensible heat which it attains during compression, and is brought nearly to the temperature of the surrounding air.

During this time the valve  $s$  of the cylinder B opens and permits a certain amount of air equal in weight to that which is expelled from A, to pass from the reservoir into the cylinder producing a certain amount of work. Then the valve  $s$  closes,—the air in the cylinder B expands producing again work which may be deducted from the work of compression and the temperature is lowered. When the piston B reaches the upper limit of its stroke, the valve  $s'$  opens and the cooled air as the piston descends escapes by the tube T.

The cooling experienced by the air, during compression, by contact with the cooled sides of the cylinder is scarcely sensible.

The machine therefore acts under conditions set forth in § 2 and we know that its useful effect cannot exceed the value

$$A \frac{T_0}{T_1 - T_0} \quad \text{or} \quad A \frac{T_2}{T_0 - T_2}$$

By means of the adjustable cams we can regulate at will the action of the valves  $s$  and  $s'$ . If we shorten the time of admission into the cylinder B, the pressure will increase in the reservoir; for the amount flowing into B should be equal to that forced into the reservoir from A. The temperature of the air expelled will then be less. If, on the contrary, we increase the time of admission the reservoir pressure will diminish, and the temperature of outflowing air will be increased.

The apparatus presents then this important peculiarity—that we can vary the useful effect of the machine at will, through wide limits.

As the air leaves B, at the pressure of the atmosphere, the minimum limit of pressure is established, below which the

expansion cannot be pushed, and which is controlled by the relative dimensions of the two cylinders.

We will proceed to calculate the cooling effect produced by this machine and the corresponding work required. We shall neglect at first the effect of waste spaces in the machine, and of watery vapor in the air.

§ 9. Let  $P_0$ ,  $t_0$  and  $T_0$  be the pressure and temperature (counted from absolute zero) of the air.

$V_0$  the volume described by the piston A.

$V_1$  the volume of air when at pressure  $P_1$ .

$V_1$  is then the volume described by the piston during the out-flow.

$m$  = weight of air whose volume passes from  $V_0$  to  $V_1$ .

$P_1$ ,  $t_1$  and  $T_1$  the pressure and temperature of compressed air delivered from A.

$V_1'$ ,  $t_1'$  and  $T_1'$  the volume and



temperature after passing into the condenser.

$V_2$  the total volume described by piston B.

$P_2$ ,  $t_2$  and  $T_2$  the pressure and temperature of the air at the end of the course of this piston.

During compression the cooling by simple contact with the sides of the cylinder is insignificant. We shall neglect this and also assume that no heat is received from the sides of the cylinder B.

#### FIRST PERIOD: COMPRESSION.

§ 10. When air is compressed without losing or gaining heat, the pressure and temperature at each instant bear the relation to each other expressed by the equation

$$P_0 V_0^k = P_1 V_1^k \quad (1)$$

in which  $k$  is the ratio of specific heat of constant pressure to the specific heat of constant volume.

$$k = \frac{0.23751}{0.16844} = 1.41$$

Gay Lussac's law affords,

$$P_0 V_0 = RmT_0 \quad (2)$$

and  $P_1 V_1 = RmT_1 \quad (3)$

From equations 1 2 and 3 we deduce

$$\frac{T_1}{T_0} = \left(\frac{P_1}{P_0}\right)^{\frac{k-1}{k}} \quad (4)$$

$$\frac{T_1}{T_0} = \left(\frac{V_0}{V_1}\right)^{k-1} \quad (5)$$

The work of the resistance to compression and outflow is

$$W_r = \frac{k}{k-1} (P_1 V_1 - P_0 V_0). \quad (6)$$

We have elsewhere

$$\frac{k}{k-1} = \frac{kc}{AR}$$

$c$  being the specific heat of air of constant volume.

Equation (6) then becomes

$$W_r = \frac{mkc}{A} (T_1 - T_0). \quad (7)$$

#### SECOND PERIOD: COOLING.

The air is cooled in the condenser under constant pressure. The volume

changes from  $V_1$  to  $V_1'$ , and the temperature from  $t_1$  to  $t_1'$ .

we have; 
$$V_1' = V \frac{T_1'}{T} \quad (8)$$

and the quantity of heat imparted to the water of the condenser is;

$$Q_1 = mkc(T_1 - T_1') \quad (9)$$

If  $T_1' = T_0$  then  $R_1 = AW_r$

### THIRD PERIOD; EXPANSION.

The volume  $V_1'$  of air enters the cylinder B yielding an amount of work equal to  $P_1 V_1'$ . It expands from  $V_1'$  to  $V_2$  without gain or loss of heat. We have then:

$$P_1 V_1'^k = P_2 V_2^k, \quad (10)$$

$$P_1 V_1' = RmT_1', \quad (11)$$

$$P_2 V_2 = RmT_2, \quad (12)$$

whence 
$$T_2 = T_1' \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}}. \quad (13)$$

The work performed by the air is

$$W_m = \frac{k}{k-1} (P_1 V_1' - P_2 V_2) \quad (14)$$

or 
$$W_m = \frac{mkc}{A} (T_1' - T_2) \quad (15)$$

The resistances to be overcome by external force amount to

$$W_r - W_m = \frac{mkc}{A} [(T_1 - T_1') - (T_0 - T_2)]. \quad (16)$$

If the machine works properly, the final pressure  $P_2$  should be equal to the atmospheric pressure.

The equations (10) (12) and (13) give

$$\text{or} \quad \left. \begin{aligned} \frac{V_2}{V_1'} &= \frac{V_0}{V_1} \\ \frac{V_2}{V_0} &= \frac{T_1'}{T_1} \end{aligned} \right\} \quad (17)$$

$$\text{and} \quad \frac{T_2}{T_1'} = \frac{T_0}{T_1} \quad (18)$$

Equation (17) expresses the ratio which should exist between the volumes of the two cylinders, in order that the air be finally expelled at atmospheric pressure, after having been compressed by a force  $P_1$ .

The negative heat (cooling), produced by the apparatus, is the quantity of heat necessary to restore the air from the temperature  $t_1$  to the temperature  $t_0$ , under constant pressure.

$$\text{or } \left. \begin{aligned} Q &= mkc(T_0 - T_2) \\ Q &= mkcT_0 \left(1 - \frac{T_1'}{T_1}\right) \end{aligned} \right\} \quad (19)$$

§ 11. Since a given weight of air is restored, at the end of the operation, to the same temperature and pressure it had at the beginning it follows, that it has been through a perfect cycle and we have from the mechanical theory of heat;

$$Q_1 = A(W_r - W_m) + Q$$

The theoretical performance of the machine is, calling it  $u$ ,

$$u = \frac{Q}{W_r - W_m} = A \cdot \frac{T_0 - T_2}{(T_1 - T_1') - (T_0 - T_2)},$$

$$u = A \cdot \frac{1}{\frac{T_1 - T_1'}{T_0 - T_2} - 1}$$

and as we have from equation (18)

$$\frac{T_1 - T_1'}{T_0 - T_2} = \frac{T_1}{T_0} = \frac{T_1'}{T_2}$$

we get finally

$$u = A \cdot \frac{T_0}{T_1 - T_0} = A \cdot \frac{T_2}{T_1' - T_2}, \quad (20)$$

a result already found in § 3 by suppos-

ing  $T_1' = T_0$ . If  $T_1 > T_0$  the useful effect is diminished.

The efficiency of the machine will be all the greater as  $T_1$  approaches in value to  $T_0$ ; that is to say as it is urged at a lower pressure into the reservoir. But as we lower the pressure of working, the quantity of negative heat produced diminishes also and becomes nothing when  $T_1' = T_1$ .

The necessary driving power  $W_r - W_m$  which we proceed to calculate, should be augmented by the passive resistances.

If we consider the refrigerating machine as composed of two distinct machines driven by the same shaft, we are led to consider that the work of the passive resistances is proportional not to the final work  $W_r - W_m$  but rather to the sum of the work developed in the two cylinders  $W_r + W_m$ . Considering the simplicity of the machine, the small amount of friction, and the absence of a stuffing box, we can admit that the work of the passive resistances should not exceed eight per cent of the above total work.

The resistance of the machine is then  $1.08W_r - 0.92W_m$ .

The following table gives the amount of refrigeration obtained, and the work expended, by passing a cubic meter of dry air through the machine; the pressures in the reservoir varying from  $1\frac{1}{2}$  to  $4\frac{1}{2}$  atmospheres. The temperature of the external air is taken at  $15^\circ$ ; the temperature of the air leaving the condenser at  $18^\circ$ ; temperature of the water about  $13^\circ$   $V_0=1$ ,  $T_0=288$  and  $m=1^k.266$ .

§ 12. An examination of the table shows the enormous influence that the passive resistances exert upon the efficiency of air machines. It is one of the consequences of the inherent cumbrousness which follows from the use of this body in a thermic machine.

The useful effect produced is not increased in proportion to the increase of pressure. It is of no advantage to employ pressures higher than about  $4\frac{1}{2}$  atmospheres. Aside from the diminution of efficiency of the air at high pressures, a loss is occasioned by heat developed in

| $P_1$<br>(Atmospheres.) | Temperature of air<br>after compression.<br>$t_1$ . | Temperature of<br>outflowing air.<br>$t_2$ . | Diminution<br>obtained.<br>$t_0 - t_2$ . | Negative calories<br>obtained. | Work expended,<br>theoretical<br>kilogrammeters. | Work expended,<br>effective. | No. of negative calories developed. |                                              |                                   |                              |
|-------------------------|-----------------------------------------------------|----------------------------------------------|------------------------------------------|--------------------------------|--------------------------------------------------|------------------------------|-------------------------------------|----------------------------------------------|-----------------------------------|------------------------------|
|                         | degrees                                             | degrees                                      | degrees                                  | cal.                           |                                                  |                              | Per<br>kilogrammeter,<br>theoretic. | Per horse power<br>per hour,<br>theoretical. | Kilogrammeter<br>really expended. | Per horse power<br>per hour. |
| $1\frac{1}{2}$          | 51.04                                               | -14.36                                       | 29.36                                    | 8,548                          | 454.26                                           | 1.070,5                      | cal.<br>0,01882                     | cal.<br>5.081, 4                             | cal.<br>0,007985                  | 2.156                        |
| 2                       | 79.31                                               | -35.12                                       | 50.12                                    | 14,591                         | 1.381,26                                         | 2.481,6                      | 0,01056                             | 2.851, 2                                     | 0,00588                           | 1.587                        |
| $2\frac{1}{2}$          | 102.93                                              | -49.55                                       | 64.55                                    | 18,792                         | 2.515,64                                         | 3.991,1                      | 0,00747                             | 2.016, 9                                     | 0,00471                           | 1.281                        |
| 3                       | 123.39                                              | -62.58                                       | 77.58                                    | 22,586                         | 3.556,3                                          | 5.412,3                      | 0,00635                             | 1.714, 8                                     | 0,00417                           | 1.126                        |
| $3\frac{1}{2}$          | 141.57                                              | -70.84                                       | 85.84                                    | 24,991                         | 4.657.3                                          | 6.724,2                      | 0,00537                             | 1.448, 8                                     | 0,00372                           | 1.003                        |
| 4                       | 157.98                                              | -78.54                                       | 93.54                                    | 27,232                         | 5.732.5                                          | 8.097,0                      | 0,00475                             | 1.282, 6                                     | 0,00336                           | 907                          |
| $4\frac{1}{2}$          | 173.00                                              | -85.09                                       | 100.09                                   | 29,375                         | 6.778,0                                          | 9.297,0                      | 0,00433                             | 1.170, 2                                     | 0,00316                           | 853                          |



the compressor, and which extends to other working parts of the machine. We have said above that, with a given machine we can vary at will the pressure  $P_1$  by varying the length of time of the opening of the admission valve in the cylinder B. If the time be shortened the pressure and the cooling effect are both increased; and if the time be increased  $P_1$  is diminished. It is necessary that we should vary at the same time the working of the emission valve, so that it opens at the moment when the piston shall have passed through a space equal to  $V_0 \frac{T_1'}{T_1}$  corresponding to the atmospheric pressure on the inside of the expansion cylinder.

A machine whose dimensions and velocity are such that it uses 1000 cubic meters of air per hour will produce from 8.548 to 29.375 negative calories and upwards per hour, provided that the driving power varies from 4 to 34 horse power.

Practically however the efficiency of air machines is not so great as is indica-

ted by the above table as no account has yet been taken of watery vapor in the air, nor of lost spaces in the machine.

We proceed to examine the influence of these two causes of loss.

#### INFLUENCE OF MOISTURE IN THE AIR.

§ 13. This influence is not to be neglected. The vapor contained in the air condenses on the sides of the expansion cylinder, and parts with its latent heat of vaporization so that the final temperature of the air is higher than it would have been if dry.

Furthermore the snow produced from this moisture accumulates around the orifice of the cold air outlet and we cannot readily utilize the cold which is required to produce it. For these two reasons, but especially for the latter, the moisture of the air causes a notable loss.

We proceed to calculate the volume and the temperature of the air at the end of the expansion under the supposition of a known hygrometric state of the atmosphere, from which we can easily de-

duce by the tables the pressure of the vapor  $p_0$  and its weight  $\mu_1$ .

In the compression cylinder of watery vapour not being near the saturation point, and exerting a feeble pressure will behave nearly as a perfect gas; its volume and its temperature are represented by the relations  $pv^k = \text{a constant}$ , in which  $k=1.41$  and  $pv=R'mT$ ;

$$R' = \frac{R}{0.622} = 47.061.$$

The total pressure of air and vapor being represented by  $P$ , the pressure of the vapor being  $p$ , that of the air alone will be  $P-p$  and we shall have preserving our former notation:

$$P_1 V_1^k = P_0 V_0^k, \quad (21)$$

$$p_1 V_1^k = p_0 V_0^k, \quad (22)$$

$$(P_0 - p_0) V_0 = RmT_0, \quad (23)$$

$$p_0 V_0 = R' \mu_1 T_0, \quad (24)$$

$$(P_1 - p_1) V_1 = RmT_1, \quad (25)$$

$$p_1 V_1 = R' \mu_1 T_1. \quad (26)$$

The work of the resistance to compression is



$$\left. \begin{aligned} W_r &= \frac{k}{k-1} (P_1 V_1 - P_0 V_0) \\ \text{or } W_r &= \frac{A}{k} (mc + \mu_1 c') (T_1 - T_0) \end{aligned} \right\} \quad (27)$$

$c'$  is the specific heat under constant volume of the superheated vapor

$$c' = 0.3407.$$

After cooling the volume becomes

$$V'_1 = V_1 \frac{T'_1}{T_1} \quad (28)$$

and we have

$$p_1 V'_1 = R' \mu_1 T'_1.$$

From equations 21 and 22 we can deduce the pressure in the reservoir.

We can determine by examining a table of tensions of saturated steam whether the pressure  $p_1$  is greater or less than the pressure which corresponds to the temperature  $T'_1$ . If it be less the air will not be saturated with vapor when leaving the condenser, and the heat absorbed by the latter will be:

$$Q_1 = k(mc + \mu_1 c') (T_1 - T'_1)$$

If the pressure  $p_1$  is greater than the

pressure  $p_1'$ , corresponding to the temperature  $T_1'$  for saturated steam, there will be a condensation of some of the vapor in the condenser; the amount condensed will be

$$\mu_1(1-x_1')$$

and the pressure of the vapor entering into the cylinder B will be  $p_1'$ , that of the air being  $P_1 - p_1'$ .

We shall have also :

$$x_1' = \frac{p_1'}{p_1} = \frac{p_1'}{p_0} \cdot \frac{P_0}{P_1}$$

We see that the quantity of vapor not condensed by the cooling, and passing into the expansion cylinder, will continually diminish in proportion as the working pressure is raised. The influence of the humidity in the air will therefore be less as the pressure is made greater.

The weight of the mixture of air and vapor, which is  $m + \mu_1$  if there is no condensation in the cooler or  $m + \mu_1 x_1'$  if there is a condensation, is carried into the cylinder B where it encounters the surfaces cooled during the preceding

stroke. We can neglect the influence of these cold surfaces upon the air alone, but not upon the mixture of air and vapor. The latter is converted into frost which releases a certain amount of heat to be imparted to the metal, and which during the expansion is restored to the air.

Suppose at first that there is no condensation in the cooler, there is conveyed to the cylinder a weight  $\mu_1$  of saturated, or nearly saturated, vapor at the temperature  $T_1'$ . We may assume, considering the very low temperature of the surfaces, that all the vapor is condensed here; it will disengage a quantity of heat  $C$ , which is approximately equal to  $\mu_1(r_1' + 79)$ .  $r_1'$  being the latent heat of the vapor corresponding to the temperature  $t_1'$ , 79 is the latent heat of water released on freezing.

The heat  $C$  is gradually restored to the air during expansion.

The pressure of the air becomes  $P_1$ , and the volume introduced into the cylinder is

$$V_1'' = \frac{RmT_1'}{P_1}.$$

The differential equation of the work is

$$\begin{aligned} \frac{c}{A} m dT + \frac{c_1}{A} \mu_1 dT - \frac{dC}{A} &= -PdV \\ &= -RmT \frac{dV}{V}; \end{aligned}$$

$c_1$  being the specific heat of ice,  $=0.5$

$$\text{or } \left( \frac{c}{AR} m + \frac{c_1}{AR} \mu_1 \right) \frac{dT}{T} - \frac{dC}{ART} = -m \frac{dV}{V}.$$

We do not know the law of relation between  $C$  and  $T_1$ , that is, how to communicate to the air the heat released from the water and ice formed. We are forced to make a hypothesis which is not rigorously exact, but which is sufficiently approximate.

We will suppose that the transmission is proportioned to the fall of temperature, and therefore that

$$dC = -\mu\gamma dT$$

in which

$$\gamma = \frac{r_1' + 79}{T_1' - T_1},$$

whence we have;

$$\frac{1}{AR} (mc + \mu_1 c_1 + \mu_1 \gamma) \frac{dT}{T} = -m \frac{dV}{V}$$

integrating we get

$$\frac{c}{AR} \left( 1 + \frac{\mu_1 c_1 + \mu_1 \gamma}{mc} \right) l \frac{T'_1}{T_2} = l \frac{V_2}{V_1'}$$

$$\text{or } \frac{1}{k-1} \left( 1 + \frac{\mu_1 c_1 + \mu_1 \gamma}{mc} \right) l \frac{T'_1}{T_2} = l \frac{V_2}{V_1'} \quad (29)$$

we have furthermore

$$P_0 V_2 = RmT_2,$$

$$P_1 V''_1 = RmT'_1,$$

whence

$$\frac{T'_1}{T_2} = \frac{P_1 V''_1}{P_0 V_2}.$$

Equation. 29 can then be written;

$$\frac{1}{k-1} \left( k + \frac{\mu_1 c_1 + \mu_1 \gamma}{mc} \right) l \frac{T'_1}{T_2} = l \frac{P_1}{P_0}. \quad (30)$$

We can obtain the value of  $T_2$  by successive approximations.

An approximate value for  $T_2$  is found to be

$$T_2 = \frac{\left\{ mkc + \mu_1 c_1 - \frac{(k-1)mc}{2} l \frac{P_1}{P_0} \right\} T'_1 + \mu_1 (r'_1 + 79)}{mkc + \mu_1 c_1 + \frac{(k-1)mc}{2} l \frac{P_1}{P_0}}$$



Suppose now that condensation occurs in the cooler, we find by the tables the pressure of  $p_1'$  of saturated vapor of temperature  $T_1'$  and we can deduce the weight of the vapor condensed in the cooler.

We shall have then;

$$C = \mu_1 x_1' (r' + 79)$$

and 
$$\gamma = x_1' \frac{r_1' + 79}{T_1' + T_2}$$

The equations 29 and 30 apply in this case as in the preceding.

The quantity of disposable negative heat is;

$$Q = mke(T_0 - T_2) \quad (31)$$

since we suppose the negative heat of the snow formed to be lost.

Finally the work produced by the expansion is;

$$W_m = P_1 V_1'' + \frac{mc}{A} \left( 1 + \frac{\mu_1 c_1 + \mu_1 \gamma}{mc} \right) (T_1' - T_2) - P_0 V_2 \quad (32)$$

$$\text{or } W_m = \frac{mke + \mu_1 (c_1 + \gamma)}{A} (T_1' - T_2) \quad (33)$$

If there is a condensation in the cooler,

we should replace  $\mu_1$  in equations 32 and 33 by  $\mu_1 x_1'$ .

§ 14. The following table gives the cooling and general effect obtained from a cubic meter of air supposing a hygrometric state of  $\frac{1}{2}$  and a temperature of  $15^\circ$ . The weight of the air is then 1.<sup>k</sup> 2157 instead of 1.<sup>k</sup> 226 which is the weight of dry air at this temperature.

We have also  $p_s = 85.<sup>k</sup> 8$  and  $\mu_1 = 0.<sup>k</sup> 00626$ .

| Pressure<br>atmospheres. | Temperature<br>in<br>compressor. | Temperature<br>of expelled air. | Cooling obtained.<br>$t_0 - t_2$ . | Negative calories. | Theoretic work,<br>kilogrammeters. | Effective work<br>expended. | No. of negative calories<br>obtained. |                                           |                                 |                               | Weight of vapor<br>carried into<br>expansion cylinder. |
|--------------------------|----------------------------------|---------------------------------|------------------------------------|--------------------|------------------------------------|-----------------------------|---------------------------------------|-------------------------------------------|---------------------------------|-------------------------------|--------------------------------------------------------|
|                          | degrees                          | degrees                         | degrees                            | cal.               |                                    |                             | Per<br>kilogrammeter,<br>theoretic.   | Per theoretic<br>horse power<br>per hour. | Per effective<br>kilogrammeter. | Per effective<br>horse power. |                                                        |
| $1\frac{1}{2}$           | 51.04                            | — 0.43                          | 15.43                              | 4,455              | 291                                | 981                         | 0.01531                               | 4.134                                     | 0.00454                         | 1.226                         | 0.00626                                                |
| 2                        | 79.31                            | — 21.70                         | 36.70                              | 10,600             | 1,257                              | 2,429                       | 0.00843                               | 2.276                                     | 0.00436                         | 1.177                         | 0.00626                                                |
| $2\frac{1}{2}$           | 102.93                           | — 37.25                         | 52.25                              | 15,090             | 2,286                              | 3,843                       | 0.00660                               | 1.782                                     | 0.00393                         | 1.061                         | 0.00615                                                |
| 3                        | 123.39                           | — 50.80                         | 65.80                              | 18,997             | 3,486                              | 5,354                       | 0.00545                               | 1.472                                     | 0.00355                         | 959                           | 0.00504                                                |
| $3\frac{1}{2}$           | 141.57                           | — 61.53                         | 76.53                              | 22,095             | 4,592                              | 6,730                       | 0.00481                               | 1.299                                     | 0.00328                         | 886                           | 0.00439                                                |
| 4                        | 157.98                           | — 70.58                         | 85.58                              | 24,710             | 5,674                              | 8,050                       | 0.00435                               | 1.176                                     | 0.00307                         | 829                           | 0.00384                                                |
| $4\frac{1}{2}$           | 173.00                           | — 78.26                         | 93.26                              | 26,928             | 6,714                              | 9,304                       | 0.00409                               | 1.104                                     | 0.00290                         | 783                           | 0.00342                                                |

In comparing this table with the table of § 11 we see that the influence of the humidity of the air upon the results obtained is the greater when the pressure is low. We have made a similar remark in reference to the passive resistances. The theoretical advantage therefore of low pressures is practically much diminished by these causes of loss.

It is possible to neutralize almost completely the influence of moisture in the air. To accomplish this it would suffice to employ the air after it had produced its cooling effect and had parted with its moisture. It would be necessary to make the refrigerating machine a closed machine, making the same quantity of air serve indefinitely. The cooling would be produced by causing the cooled air to pass through an apparatus surrounded by some liquid not easily frozen, such as a solution of calcium or magnesium chloride. A part of the negative calories would thus be used, as well as by direct contact, and so many as are not used would not be lost, as the air

passes directly to the compressor A, not at  $15^\circ$  as before, but  $\alpha - 8^\circ$  or  $-10^\circ$  of temperature. We think that it is only in this way that we can improve the air machine so that it can compare favorably with the machines using a liquefrable gas.

#### INFLUENCE OF WASTE SPACES.

§ 15. We will suppose the air to be dry in order to avoid complexity in our calculations.

Preserving our previous notation and calling  $v$  the amount of useless space in the compression cylinder, and  $v'$  that of the expansion cylinder;  $\mu$  the weight of air enclosed in the space  $v$  at the end of the compression, we have;

$$P_0(V_0 + v)^k = P_1(V_1 + v)^k \quad (34)$$

$$P_0(V_0 + v) = R(m + \mu)T_0 \quad (35)$$

$$P_1V_1 = RmT_1 \quad (36)$$

$$Pv_1 = R\mu T_1 \quad (37)$$

$m$  being the weight of dry air driven out of the compressor.

Equations (34), (35), (36) and (37) give by elimination of  $\mu$

$$T_1 = T_0 \left( \frac{V_0 + v}{V_1 + v} \right)^{k-1} \quad (38)$$

$$\text{and} \quad T_1 = T_0 \left( \frac{P_1}{P_0} \right)^{\frac{k-1}{k}} \quad (39)$$

The work of resistance to compression, taking account of the work restored to the piston as it begins to ascend, by the air in the waste space, expanding from  $P_1$  to  $P_0$ , is;

$$W_r = \frac{k}{k-1} (P_1 V_1 - P_0 V_0) + \frac{1}{k-1} P_0 v \frac{V_0 - V_1}{V_1 + v}; \quad (40)$$

For the cooling period;

$$V_1' = V_1 \frac{T_1'}{T_1} \quad (41)$$

$$\text{and} \quad P_1 V_1' = R m T_1' \quad (42)$$

The heat  $Q_1$  absorbed by the water of the condenser is;

$$Q_1 = m k c (T_1 - T_1') \quad (43)$$

PERIOD OF EXPANSION.—The air coming from the reservoir  $R'$  under pressure  $P_1$  and the temperature  $P_1'$ , should at the moment of opening of the inlet valve

cause the air in the waste space and whose volume is  $v'$ , to change its pressure from  $P_0$  to  $P_1$ . This influences the temperature  $T_1''$  of the mixture, also the weight  $m'$  of the air which passes from the reservoir into the waste space.

— The dimensions of the reservoir being very large in comparison to the waste spaces, we may assume that no change occurs either in temperature or pressure of the reservoir, while the waste spaces are filled with air at the pressure  $P_1$ .

— Calling  $\mu'$  the weight of the air enclosed in the waste space at the moment that the inlet valve opens. We have;

$$P_0 v' = R \mu' T_2; \quad (44)$$

$T_2$  being the final temperature of the expanded air.

The stored up work of this air is;

$$\frac{c}{A} \mu' T_2.$$

The weight  $m'$  of air filling the waste space, and having a temperature  $T_1'$  and a pressure  $P_1$  has a stored energy of

$$\frac{c}{A} m' T_1'.$$

After the waste space is filled, the stored up energy of the total quantity of air  $m' + \mu'$  contained there is

$$\frac{c}{A}(m' + \mu')T_1''$$

and we have furthermore;

$$P_1 v' = R(m' + \mu')T_1''. \quad (45)$$

As we suppose there is neither loss nor gain of heat from the exterior, the difference between the stored energy of the mixture after the mass  $m'$  is introduced, and the sum of the stored energies of the masses  $m'$  and  $\mu'$  before mixing is equal to the external work performed.

This exterior work is evidently  $P_1 v_1'$ , and calling the volume of  $m'$  before its introduction into the cylinder under pressure  $P_1$  and temperature  $T_1'$  equal to  $v_1'$ , then;

$$P_1 v_1' = RmT_1'.$$

We have also

$$-\frac{c}{A} \mu T_2 - \frac{c}{A} m' T_1' + \frac{c}{A} (m' + \mu') T_1'' = RmT_1',$$



Replacing  $\frac{c}{A}$  by  $\frac{R}{k-1}$  and combining with equations 44 and 45

$$m' = \frac{(P_1 - P_0)v'}{kRT'} \quad (46)$$

$$\left. \begin{array}{l} \text{and } T_1'' = \frac{km'T_1' + \mu'T_2}{m' + \mu'} \\ \text{or } T_1'' = \frac{kP_1T_1'T_2}{P_1T_2 + P_0(kT_1' - T_2)} \end{array} \right\} \quad (47)$$

When the inlet valve closes, the piston has described a volume  $V_1''$ , which has been filled by the weight  $m''$  of air at pressure  $P_1$  and temperature  $T_1'$ . We have then;

$$m' + m'' = m$$

There is no external work performed upon the total mass of air, since the negative work of the piston  $P_1V_1''$  is exactly equal to the positive work exerted by the air of the reservoir. The weights and temperatures of the air at the beginning and the end of the introduction possess the following relations:

$$\begin{aligned} \frac{c}{A}(m' + \mu)T_1'' + \frac{c}{A}m''T_1' \\ = \frac{c}{A}(m' + m'' + \mu')T_1'''. \end{aligned}$$

$T_1'''$  being the temperature at the end of the introduction.

This equation gives;

$$\left. \begin{aligned} T_1''' &= \frac{(m' + \mu')T_1'' + m''T_1'}{m + \mu'} \\ \text{or} \quad T_1''' &= \frac{P_1(V_1' + v') - \frac{1}{k}(P_1 - P_0)v'}{P_1V_1'T_2 + P_0v'T_1'} T_1'T_2 \end{aligned} \right\} \quad (48)$$

we also have

$$\begin{aligned} P_1(V_1'' + v') &= R(m + \mu')T_1''' \\ \text{or} \quad P_1(V_1'' + v') &= P_1(V_1' + v') \\ &\quad - \frac{1}{k}(P_1 - P_0)v'; \quad (49) \end{aligned}$$

$V_1'$  is given equations 38 and 41. Equation 49 gives the value of  $V_1''$ .

The inlet valve being closed, the mass of air  $m + \mu$  which is at pressure  $P_1$  and temperature  $T_1'''$  expands without gain or loss of heat since we neglect the

influence of the sides of the cylinder. At the end of the stroke, this volume becomes  $V_2 + v'$ , its temperature  $T_2$  and its pressure  $P_2$ . We have then

$$\left. \begin{aligned} P_2(V_2 + v')^k &= P_1(V_1' + v')^k \\ \text{or} \\ P_2(V_2 + v')^k &= P_1 \left\{ (V_1' + v') - \frac{1}{k} \left( 1 - \frac{P_2}{P_1} \right) v' \right\}^k \end{aligned} \right\} \quad (50)$$

and

$$P_2(V_2 + v') = R(m + \mu')T_2 \quad (51)$$

Equations 50 and 51 give  $V_2$  and  $T_2$  if  $P_2$  be known, or  $P_2$  and  $T_2$  if  $V_2$  is known; this latter being the volume described by the piston of cylinder B.

We have

$$T_2 = T_1''' \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}}$$

When there is no waste space we have

$$T_2 = T_1' \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}}$$

As  $T_1'''$  is greater than  $T_1'$ , it results that for a given weight of air passed through the machine, at a given working

pressure, that the final temperature of the expanded air would be higher, and consequently the number of negative calories produced would be less than if there had been no waste spaces.

The work is equal to :

$$W_m = \frac{k}{k-1} (P_1 V_1' - P_2 V_2) + (P_2 - P_0) V_2 + \frac{1}{k-1} (P_0 - P_2) v' \quad (52)$$

§ 16. In order that the machine should work to the best advantage it is evidently necessary that the air should leave the cylinder at atmospheric pressure, that is, that  $P_2$  should equal to  $P_0$ . There ought then to exist a certain relation between the volume of the compression cylinder  $V_0 + v$ , the pressure in the reservoir  $P_1$  and the volume of the expansion cylinder  $V_2 + v'$  which may be determined by the above equations. To fix the dimensions of a machine we may assume  $V_0 + v$  and  $P_1$  as given, and then deduce the value of  $V_2 + v'$ .

If we make  $P_2 = P_1$  equations 50 and 51 will become

$$P_0(V_2 + v')^k = P_1 \left\{ (V_1 + v') - \frac{1}{k} \frac{P_1 - P_0}{P_1} v' \right\}$$

$$\text{and} \quad P_0 V_2 = RmT_2,$$

whence

$$V_2 + v' = (V_0 + v) \left( \frac{P_0}{P_1} \right)^{\frac{k-1}{k}}$$

$$\left( \frac{T_1'}{T_0} = \frac{1}{k} \frac{P_1 - P_0}{P_0} \frac{v'}{V_0 + v} \right). \quad (53)$$

The work is

$$\left. \begin{aligned} W_m &= \frac{k}{k-1} (P_1 V_1' - P_0 V_2) \\ \text{or} \quad W_m &= \frac{mkc}{A} (T_1' - T_2) \end{aligned} \right\} \quad (54)$$

This value for the work is the same as found in § 7, where no waste space was allowed for; only the final temperature  $T_2$  being greater for the same weight and pressure, the work of the air is less.

The work of the resistance of the machine is then :



$$\left. \begin{aligned}
 W_r - W_m &= \frac{k}{k-1} [P_1(v_1 - v_1') \\
 &\quad - P_0(v_0 - v_2)] + \frac{k}{k-1} P_0 v \frac{V_0 - V_1}{V_1 + v} \\
 \text{or } W_r - W_m &= \frac{m k c}{A} \\
 &\quad (T_1 - T_1' - T_0 + T_2)
 \end{aligned} \right\} (55)$$

The negative heat produced is

$$Q = m k c (T_0 - T_2) \quad (56)$$

$$Q_1 - Q = W_r - W_m \quad (57)$$

The performance of the machine is

$$u = \frac{T_0 - T_2}{T_1 - T_1' - T_0 + T_2}$$

$$\text{or } \frac{T_1 - T_1'}{T_1 - T_1'''} \frac{T_0}{T_1 - T_0} \quad (58)$$

As  $T_1'''$  is greater than  $T_1$ , the useful effect is less than if there had been no waste space.

§ 17. The following table exhibits the results of a machine having waste space of 4 per cent. of the volume described by the pistons. The amount of air used being a cubic meter at  $15^\circ$ , and weighing

| $P_1$<br>(Atmospheres.) | Temperature<br>of outflow<br>from compressor. | Temperature<br>of final outflow. | Cooling of air. | Negative calories. | Theoretical work. | Effective work. | Negative calories developed.    |                                           |                                 |                                           |
|-------------------------|-----------------------------------------------|----------------------------------|-----------------|--------------------|-------------------|-----------------|---------------------------------|-------------------------------------------|---------------------------------|-------------------------------------------|
|                         | degrees                                       | degrees                          | degrees         | cal.               |                   |                 | Per theoretic<br>kilogrammeter. | Per theoretic<br>horse power<br>per hour. | Per effective<br>kilogrammeter. | Per effective<br>horse power<br>per hour. |
| $1\frac{1}{2}$          | 51.04                                         | -14.17                           | 29.17           | 8,492              | 478               | 1.150           | 0.017777                        | 4.800                                     | 0.007385                        | 1.984                                     |
| 2                       | 79.31                                         | -34.76                           | 49.76           | 14,486             | 1,426             | 2.582           | 0.010160                        | 2.743                                     | 0.005611                        | 1.515                                     |
| $2\frac{1}{2}$          | 102.93                                        | -49.17                           | 64.17           | 18,682             | 2,563             | 4.094           | 0.007290                        | 1.968                                     | 0.004563                        | 1.231                                     |
| 3                       | 123.39                                        | -60.33                           | 75.33           | 21,931             | 2,711             | 5.555           | 0.005910                        | 1.596                                     | 0.003948                        | 1.066                                     |
| $3\frac{1}{2}$          | 141.57                                        | -69.21                           | 84.21           | 24,516             | 4,859             | 6.970           | 0.005045                        | 1.362                                     | 0.003517                        | 950                                       |
| 4                       | 157.98                                        | -76.57                           | 91.57           | 26,658             | 5,976             | 8.321           | 0.004470                        | 1.207                                     | 0.003204                        | 864                                       |
| $4\frac{1}{2}$          | 173.00                                        | -82.78                           | 97.78           | 28,468             | 7,063             | 9.617           | 0.004031                        | 1.088                                     | 0.002960                        | 799                                       |

1<sup>k</sup> 226. In the cooler the air is brought to 18°.

By comparing these results with those of § 11, we see that the effect of waste spaces is by no means to be neglected since it results in a loss of about 100 calories for each theoretic horse power per hour.

§ 18. We can neutralize the influence of waste space by closing the outlet valve of cylinder B before the end of the stroke, so as to compress the air in this space; the stroke of the piston being exactly determined, the air in the waste space may be brought at the opening of the inlet valve to the temperature  $T_1'$  and the pressure  $P_1'$ .

In this case the equations 34 and 43 apply without change.

During the period of expansion we have:

$$P_2(V_2 + v')^k = P_1(V_1' + v')^k \quad (59)$$

$$P_2(V_2 + v') = R(m + \mu')T_2 \quad (60)$$

$$P_1V_1 = R\mu'T_1' \quad (61)$$

whence



$$\frac{T_2}{T_1'} = \left( \frac{V_2 + v'}{V_1' + v'} \right)^{k-1} = \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \quad (62)$$

The work restored by piston B is to make allowance for the compression of air in the waste space from the pressure  $P_0$  to  $P_1$ :

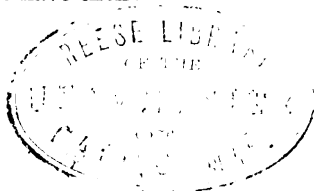
$$\left. \begin{aligned} W_m = & \frac{k}{k-1} (P_1 V_1' - P_2 V_2) - \\ & (P_0 - P_2) \frac{k}{k-1} P_0 v' \frac{V_0 - V_1}{V_1 + v'} \\ & + \frac{1}{k-1} (P_0 - H_2) v' \end{aligned} \right\} \quad (63)$$

or

$$\begin{aligned} W_m = & \frac{mkc}{A} (T_1' - T_2) + (k-1) \frac{mc}{A} T_2 \\ & \left( 1 - \frac{P_0}{P_2} \right) - (k-1) \frac{\mu' c}{A} \left( \frac{P_0}{P_2} T_2 - T_2' \right); \end{aligned}$$

$T_2'$  being the temperature of the air in the cylinder at the moment compression commences before the end of the stroke.

We have then:



$$\left. \begin{aligned} W_m &= \frac{k}{k-1} \\ &[P_1(V_1 - V_1') - P_0 V_0 + P_2 V_2] + \\ &+ (P_0 - P_2) V_2 + \frac{k}{k-1} P_0 (v - v') \\ &\frac{V_0 - V_1}{V_1 + v} - \frac{1}{k-1} (P_0 - P_2) v'. \end{aligned} \right\} \quad (64)$$

When the machine is well regulated, the final pressure  $P_2 - P_0$  and the equations 63 and 64 become

$$\begin{aligned} W_m &= \frac{k}{k-1} (P_1 V_1' - P_0 V_2) \\ &+ \frac{k}{k-1} P_0 v' \frac{V_0 - V_1}{V_1 - v} \end{aligned} \quad (65)$$

or 
$$W_m = \frac{m k c}{A} (T_1' - T_2)$$

and

$$\left. \begin{aligned} W_r - W_m &= \frac{k}{k-1} \\ &[P_1(V_1 - V_1') - P_0(V_0 - V_2)] + \\ &+ \frac{k}{k-1} \cdot P_0 (v - v') \frac{V_0 - V_1}{V_1 + v}. \end{aligned} \right\} \quad (66)$$

We have also :

$$\frac{V_0 + v}{V + v} = \frac{V_2 + v'}{V_1' + v'}. \quad (67)$$

We see that in equation 66 the term relating to waste spaces disappears if we make  $v=v'$ . The equation then becomes

$$W_r - W_m = \frac{k}{k-1} [P_1(V_1 - V_1') - P_0(V_0 - V_2)]$$

The volume  $V_2 + v'$  is determined by means of equations 39, 41 and 67 when the pressure  $P_1$  is known.

Reciprocally when  $V_0$ ,  $v$ ,  $V_2$  and  $v'$  are known (the dimensions of the machine) then  $V_1'$  is readily found, and consequently  $P_1$  and  $T_1$ , the pressure and temperature at the end of the stroke in cylinder B to insure the escape of the air at the atmospheric pressure.

§ 19. It was remarked in § 5 that the efficiency of the machine could be notably improved by cooling the air in the interior of the compressor cylinder.

This result can be accomplished, in part at least, if not completely, by means of a jet of water, such as is employed in compressed air engines.

We will proceed to calculate the work necessary for the compression in this

particular case, neglecting the effect of waste spaces.

Let  $m$  be the weight of dry air occupying the volume  $V_0$ . Let  $M$  represent the weight of water injected together with the amount of moisture in the air, and  $Mx$  the weight of the vapor at any instant.

The dilatation or compression of the mixture of the vapor and air is effected in such manner as to satisfy the differential equation :

$$mc dt + M(dq + dx\rho) = -APdV. \quad (69)$$

which expresses the fact that variations in the internal heat of the mixture equal the variations of work accomplished.

We have also

$$dq = c_1 dt,$$

$c$  being the specific heat of water.

The differential equation can then be written

$$(mc + Mc_1)dt = -Mdx\rho - A(P - p)dV - ApdV$$

$p$  being the tension of the vapor, and  $P$  that of the mixture.

But  $x\rho = xr - Apxu$   
 $dx\rho = dxr - Apxdu - Axudp.$   
 and  $dV = Mdxu$

$\rho$  is the latent heat of the vapor,  
 $r$  is the heat of vaporization,  
 $u$  is the increase of volume of a kilogram  
 of water vaporized.

We know furthermore that

$$Axu \frac{dp}{dt} = \frac{xr}{T}.$$

We have then

$$Mdx\rho + ApxdV = Mdxr - \frac{xrdt}{T}$$

or 
$$\frac{Mdx\rho + ApxdV}{T} = Md \frac{xr}{T},$$

from which we deduce

$$(mc + Mc_1) \frac{dt}{T} + Arm \frac{dV}{V} = -Md \frac{xr}{T}.$$

Integrating between the limits  $T_1$  and  $T_0$ ,

$$(mc + Mc_1) l \frac{T_0}{T_1} + M \frac{x_0 r_0}{T_0} - M \frac{x_1 r_1}{T_1} + ARml \frac{V_0}{V_1} = 0, \quad (70)$$

$$Mx_0 = \frac{V_0}{u_0} \text{ and } Mx_1 = \frac{V_1}{u_1};$$

$\frac{1}{u_0}$  and  $\frac{1}{u_1}$  are very nearly the reciprocals of the vapor densities under the pressures  $p_0$  and  $p_1$ .

We have furthermore

$$V_1 = Rm \frac{T_1}{P_1 - p_1}.$$

Equation 70 will give  $M$  when  $T_1$  and  $T_0$  are known.

$$\begin{aligned} AW_r &= mc(T_1 - T_0) \\ &+ M(q_1 - q_0 + x_1 \rho_1 - x_0 \rho_0) + A(P_1 V_1 - P_0 V_0) \\ \text{or } AW_r &= mkc(T_1 - T_0) \\ &+ M(q_1 - q_0 + x_1 r_1 - x_0 r_0) \end{aligned} \quad (71)$$

This equation gives the work of resistance when  $M$  has become known.\*

\* The two equations 70 and 71, which express the relations between the volumes and the temperatures of a mixture of air and vapor, which is compressed or dilated, and which determine also the value of the work, are applicable to the Mekarski motor.

In this machine, which is designed to employ compressed air, the air is reheated just before it is introduced into the cylinder by being forced through water, having a temperature of 100° to 150°. The cylinder then contains air and saturated vapor, heated to a mean temperature of 100°.

In M. Colladon's compressors, into which a spray of water is injected, the air being compressed to four atmospheres, the temperature  $T_1$  does not rise above  $50^\circ$  centigrade, the external air being about  $50^\circ$ .

We deduce then

$$V_1 = 0.28429 \text{ cu. metres}$$

$$M = 0.57212$$

$$W_r = 15.291 \text{ kilogrammeters.}$$

When the compression is effected without external cooling, we found in § 11 that the work of compression = 17.649 kilogrammeters, which shows a gain in the above process of about 13 per cent.

It remains to determine  $W_r$  for any pressure without any known value of  $T_1$ .

When a certain volume of air is dilated or compressed, with or without the addition of heat, the relation of pressure to volume is expressed by the equation

$$PV^a = \text{a constant.}$$

---

The weight  $M$  of equations 70 and 71 is then the weight of the vapor contained in air, saturated at the temperature at which it leaves the hot water.

$$\frac{V_1}{V_0} = \left( \frac{P_0 - p_0}{P_1 - p_1} \right)^{\frac{1}{a}} \quad (72)$$

and 
$$\frac{T_1}{T_0} = \left( \frac{P_1 - p_1}{P_0 - p_0} \right)^{\frac{a-1}{a}} \quad (73)$$

which gives

$$\frac{a-1}{a} = \frac{\log T_1 - \log T_0}{\log(P_1 - p_1) - \log(P_0 - p_0)}; \quad (74)$$

$T_1$ , having been found by experiment, equation gives  $a$ .

Making 74  $P_1 = 4$  atmospheres,  $T_1 = 323^\circ$  and  $T_0 = 288^\circ$  we find  $a = 1.0912$ .  $a$  being thus determined equation 73 will give  $M_1$ . Only  $p_1$  being a function of  $T_1$ , the latter must be found by successive approximations.

Equation 70 gives

$$Mc_1 = 0.4343 \frac{\frac{V_0 r_0}{u_0 T_0} - \frac{V_1 r_1}{u_1 T_1}}{\log \frac{T_1}{T_0}} + 0.5888 m.$$

$r_0$ ,  $u_0$ ,  $r_1$  and  $u_1$  are furnished by the tables.

Finally we obtain  $W_r$  by equation 71.



The saturated air in passing into the cooler is reduced in temperature from  $T_1$  to  $T_1'$ , and a portion of the vapor is condensed. The weight of vapor remaining and introduced into the expansion cylinder is:

$$\mu_1 = \frac{V_1'}{u_1'}$$

$\frac{1}{u_1'}$ , being the density of the vapor corresponding to the temperature  $T_1'$ .

We will calculate again the cooling produce by the expansion and the work as explained in § 13.

§ 20. The following table exhibits the results obtained from a cubic meter of air saturated at  $15^\circ$ , since the sides of the compressor cylinder are covered with water. The weight of the air is  $1^k 021$ .

| Pressures. | Temperature<br>in<br>compressor. | Temperature<br>of air going out. | Reduction<br>of<br>Temperature. | Negative calories<br>obtained. | Theoretic work<br>developed. | Work of resistance. | Effective work<br>developed. | Negative calories obtained.     |                                  |                                 |                                  | Weight of vapor<br>introduced into<br>cylinder B. |
|------------|----------------------------------|----------------------------------|---------------------------------|--------------------------------|------------------------------|---------------------|------------------------------|---------------------------------|----------------------------------|---------------------------------|----------------------------------|---------------------------------------------------|
|            | degrees                          | degrees                          | degrees                         | cal.                           |                              |                     |                              | Per theoretic<br>kilogrammeter. | Per theoretic<br>H. P. per hour. | Per effective<br>kilogrammeter. | Per effective<br>H. P. per hour. |                                                   |
| 1½         | 24,79                            | + 5,79                           | 9,21                            | 2,636                          | 189                          | 4,266               | 856                          | 0,0139                          | 3,763                            | 0,00308                         | 832                              | 0,01010                                           |
| 2          | 32,00                            | - 18,62                          | 33,62                           | 9,623                          | 709                          | 6,687               | 1,833                        | 0,01357                         | 3,663                            | 0,00525                         | 1,417                            | 0,00759                                           |
| 2½         | 37,68                            | - 37,27                          | 52,27                           | 14,962                         | 1,368                        | 9,885               | 2,953                        | 0,01094                         | 2,953                            | 0,00527                         | 1,423                            | 0,00609                                           |
| 3          | 42,38                            | - 51,30                          | 66,30                           | 18,979                         | 2,000                        | 11,940              | 3,750                        | 0,00949                         | 2,562                            | 0,00506                         | 1,366                            | 0,00509                                           |
| 3½         | 46,26                            | - 62,48                          | 77,48                           | 22,179                         | 2,636                        | 13,723              | 4,621                        | 0,00841                         | 2,270                            | 0,00480                         | 1,296                            | 0,00436                                           |
| 4          | 50,00                            | - 71,60                          | 86,60                           | 24,790                         | 3,244                        | 15,291              | 5,431                        | 0,00764                         | 2,063                            | 0,00456                         | 1,231                            | 0,00382                                           |
| 4½         | 53,13                            | - 79,40                          | 94,40                           | 27,022                         | 3,809                        | 16,672              | 6,172                        | 0,00709                         | 1,914                            | 0,00438                         | 1,182                            | 0,00340                                           |

An examination of this table and a comparison with the table of § 14 shows:

1st. That the injection of water into the interior of the compressor cylinder increases the efficiency 40 to 50 per cent.

2d. That the efficiency is at a maximum at a pressure of  $2\frac{1}{2}$  atmospheres.

3d. That it diminishes, though slowly, as we vary from this pressure.

4th. That the quantity of snow or ice produced is not greater than that which comes from the moisture of the atmosphere.

The most favorable working pressure appears to be in this case nearly 4 atmospheres, since we obtain then a sufficiently good result (24 to 25 negative calories for a cubic meter of air), with a relatively good performance of 1,200 negative calories per horse-power per hour.

Theoretically the injection of water into the compressor affords a great advantage. But it is possible that the water resulting from the condensation of vapor in the cooler does not all remain

in the reservoir, but that a portion is carried mechanically into cylinder B.

The results indicated above for the efficiency would in such a case be considerably modified, and the increase in the quantity of frozen vapor would constitute in practice a grave inconvenience.

Experiment can alone decide this question.

We have examined in the preceding pages nearly all the problems belonging to the air machine. We will pass now to the study of the second class of machines, or those which transform motive force into negative heat by the employment of a liquefiable gas.

§ 21. THE principle of these machines is the same as that of the kind described in the last chapter. The gas is compressed, then deprived of its heat, and finally caused to expand in such a manner as to lower its temperature. Only in this instance the abstraction of the heat which follows the compression, has the effect to liquefy the gas, and it is the vaporization of the resulting liquid which

produces the lowering of the temperature.

When a change of volume of a saturated vapor is made under constant pressure, the temperature remains constant. The addition or subtraction of heat, which produces the change of volume, is represented by an increase or a diminution of the quantity of liquid mixed with the vapor.

On the other hand when vapors, even if saturated, are no longer in contact with their liquids, and receive an addition of heat, either through compression by a mechanical force, or from some external source of heat, they comport themselves nearly in the same way as permanent gases, and become superheated.

It results from this property, that refrigerating machines, using a liquefiable gas will afford results differing according to the method of working, and depending upon the state of the gas, whether it remains constantly saturated, or is superheated during a part of the cycle of working.

§ 22. We will suppose first that the

gas is constantly saturated and will examine the conditions to be fulfilled under this hypothesis, and the results that may be obtained.

Employing the notation of the preceding chapter we will designate by  $m$  the weight of the gas employed,  $P_2$  and  $T_2$ , the pressure and the absolute temperature of the cooled gas,  $P_1$  and  $T_1'$ , the pressure and the absolute temperature in the condenser.

The pressures  $P_2$  and  $P_1$  are determined by the temperatures  $T_2$  and  $T_1'$ ; These are the pressures of a saturated vapor at these temperatures, and are given in Regnault's tables.

The temperature of the condenser is determined beforehand by local conditions. Depending on the surface, the interior of the condenser will exceed by  $5^\circ$  or  $10^\circ$  the temperature of the water furnished to the exterior. This latter will vary from  $11^\circ$  or  $12^\circ$  C the temperature of water from considerable depth below the surface, to  $30^\circ$  or  $35^\circ$ , the temperature of surface water in hot

climates. The volatile liquid employed in the machine ought not at this temperature to have a tension above that which can be readily managed by the apparatus.

On the other hand if the tension of the gas at the minimum temperature is too low, it becomes necessary to give to the compression cylinder large dimensions, in order that the weight of vapor afforded by a single stroke of the piston shall be sufficient to produce a notably useful effect.

These two conditions, to which may be added others; such as those depending on the greater or less facility of obtaining the liquid, upon the dangers incurred in its use either from its inflammability or unhealthfulness, and finally upon its action upon the metals, limit the choice to a small number of substances.

The gases or vapors in use, are; Sulphuric Ether, Sulphurous Oxide, Ammonia and Methylic Ether.

The following table derived from



Regnault exhibits the tensions of the vapors of these four substances at different temperatures between  $-30^{\circ}$  and  $+40^{\circ}$ . The original tables expressed the tensions in millimeters of mercury. To facilitate computation, the tensions are here given in *kilograms per square meter*.

| Tempera-<br>ture. | Sulpuric<br>Ether. | Sulphur<br>Dioxide. | Ammonia. | Methylic<br>Ether. |
|-------------------|--------------------|---------------------|----------|--------------------|
| $-40$             | —                  | —                   | 7.187    | —                  |
| $-35$             | —                  | —                   | 9.302    | —                  |
| $-30$             | —                  | 3.908               | 11.918   | 7.837              |
| $-25$             | —                  | 5.082               | 15.120   | 9.736              |
| $-20$             | 917                | 6.519               | 19.003   | 11.992             |
| $-15$             | 1.194              | 8.265               | 23.669   | 14.652             |
| $-10$             | 1.541              | 10.366              | 29.225   | 17.765             |
| $-5$              | 1.968              | 12.874              | 35.797   | 21.380             |
| 0                 | 2.493              | 15.840              | 43.475   | 25.547             |
| $+5$              | 3.129              | 19.322              | 52.405   | 30.318             |
| $+10$             | 3.894              | 23.378              | 62.707   | 35.743             |
| $+15$             | 4.808              | 28.074              | 74.504   | 41.873             |
| $+20$             | 5.891              | 33.474              | 87.925   | 48.755             |
| $+25$             | 7.164              | 39.645              | 103.073  | 56.437             |
| $+30$             | 8.651              | 46.659              | 120.083  | 64.961             |
| $+35$             | 10.377             | 54.585              | 129.054  | —                  |
| $+40$             | 12.367             | 63.496              | 160.112  | —                  |

An inspection of the table shows at once that the use of ether does not



readily lead to the production of low temperatures because its pressure becomes then very feeble.

The ether machine is, however, abandoned. Ammonia on the contrary is well adapted to the production of low temperatures; but its elastic force is very great at temperatures from  $15^{\circ}$  to  $30^{\circ}$  which are readily produced in the condenser. It is not a good aid to the transformation of mechanical force into heat, on account of the difficulty of maintaining tight joints in the apparatus, and of the influence of waste spaces at the high pressures. Methylic ether yields low temperatures without attaining too great pressures at the temperature of the condenser. Finally, sulphur dioxide readily affords temperatures of  $-10^{\circ}$  to  $-15^{\circ}$  while its pressure is only 3 to 4 atmospheres at the ordinary temperature of the condenser. These two latter substances then lend themselves conveniently for the production of cold by means of mechanical force.

§ 23. Let  $c$  be the specific heat of the liquid employed.

$q$  the quantity of heat necessary to raise 1 kilogram of the liquid from  $0^\circ$  to  $T^\circ - 273^\circ$ .

$$q = c(T - 273)$$

$\lambda$ ,  $r$ ,  $\rho$ , the total heat, the heat of vaporization, and the latent heat of the vapor considered at the temperature  $T^\circ - 273^\circ$ .

$u$ , the increase of volume of one kilogram of liquid vaporizing at  $T^\circ - 273^\circ$ .

We have by definition

$$\lambda = r + q$$

$$\rho = r = APu.$$

We will apply indices to these quantities similar to those which affect the letter  $T$  in designating the different absolute temperatures.

In order that the vapor be constantly saturated, it is necessary that the quantities of liquid and of vapor taken into the compressor at once be such that at the end of the compression all the liquid

shall be vaporized and the vapor shall not be superheated.

If we let  $x'_2$ , represent the proportion of vapor contained in the mixture at the commencement of the inflow, the work of compression will be equal to the difference in the amount of internal heat of the mixture at the beginning and end of the compression, that is to say to  $m(q'_1 - q_2 + \rho'_1 - x'_2 \rho_2)$ .

The work of the inflow into the condenser will be  $P_1 V_1$ , calling  $V_1'$  the volume occupied by a weight  $m$  of the vapor at the end of the compression, and the work of the back pressure will be  $P_2 V_2$ ,  $V_2$  being the volume occupied by the weight  $mx'_2$  of vapor.

We have also

$$V_1' = m \left( u'_1 + \frac{0,001}{\delta} \right)$$

$$\text{and} \quad V_2 = mx'_2 \left( u_2 + \frac{0,001}{\delta} \right), \quad (75)$$

$\delta$  being the density of the liquid supposed constant.

We may neglect the fraction which is very small, and write

$$\begin{aligned}V'_1 &= mu'_1, \\ V_2 &= mx'_2 u_2,\end{aligned}$$

from which we may get

$$\begin{aligned}mr'_1 &= m\rho'_1 + AP_1 V'_1, \\ \text{and} \quad mr_2 &= m\rho_2 + AP_2 V_2.\end{aligned}$$

The total work of the compression including the outflow is

$$AW_r = m(q'_1 - q_2 + r'_1 - x'_2 r_2). \quad (76)$$

As the compression follows an adiabatic curve, the quantities  $q'_1$ ,  $q_2$ ,  $r'_1$ ,  $r_2$ ,  $T'_1$ , and  $T_2$  bear the following relation:

$$\int_{T_2}^{T'_1} \frac{cdt}{T} = \frac{x'_2 r_2}{T_2} - \frac{r'_1}{T'_1},$$

or more simply,

$$\frac{r'_1}{T'_1} + cl \frac{T'_1}{T_2} = \frac{x'_2 r_2}{T_2}. \quad (77)$$

Equation (77) will give the quantity  $x'_2$ . Consequently equation (75) furnishes, when we know  $m$ , the volume  $V_2$  that the piston should describe during the aspiration in order that all the liquid should be vaporized at the end of the compression; or, inversely, the weight  $m$  may be found if  $V_2$  be given.

The vapor flows into the condenser where it is liquefied.

The heat absorbed by the water of the condenser is

$$Q_1 = mr'_1 \quad (78)$$

The liquid, then passes into the expansion cylinder where it is vaporized, producing work till it attains the pressure  $P_2$  and the temperature  $T_2$  of the refrigerant. At the end of the expansion, the weight of vapor in the mixture is  $mx_2$ .

The work, including the counter-pressure, and neglecting the work of introducing the liquid,  $p_1 \frac{0.001.m}{\delta}$ , which is very small, is;

$$AW_m = m(q'_1 - q_2 - x_2 r_2). \quad (79)$$

and the equation of the adiabatic curve is

$$\frac{x_2 r_2}{T_2} = cl \frac{T'_1}{T_2} \quad (80)$$

which determines  $x'_2$ .

The quantity of heat  $Q$  necessary to bring the mixture whose weight is

$m(1-x_2)$  of liquid and  $mx_2$  of vapor to its primitive condition, in which  $m(1-x'_2)$  is the weight of the liquid and  $mx'_2$  is the weight of the vapor, is,

$$Q = m(x'_2 - x_2)r_2$$

or by reason of equations (76) and (79)

$$Q = \frac{T_2}{T'_1} mr'_1 \quad (81)$$

The work expended is  $W_r - W_m$  and we have

$$A(W_r - W_m) = m[r'_1 - (x'_2 - x_2)r_2] = Q_1 - Q. \quad (82)$$

The theoretic performance of the machine is

$$\frac{Q}{W_r - W_m} = \frac{AQ}{Q_1 - Q} = A \cdot \frac{T_2}{T'_1 - T_2} \quad (83)$$

a result already found in section 3, and which is identical with that at which we arrived in the case of permanent or non-liquefiable gases.

§ 24. We will now take a numerical example, and consider the dimensions of the cylinders to be so regulated that a final temperature of  $-15^\circ$  is obtained, the temperature of the condenser being

+18°, and the volume of gas taken into the compressor at each stroke,  $V_1$ =one cubic meter.

The resolution of the above equations supposes a knowledge of the values of  $r$ ,  $q$ ,  $c$  and  $u$ , or  $APu$ . They have been determined directly by Regnault for sulphuric ether, but not for sulphur dioxide, ammonia and methylic ether. Availing ourselves of the experiments of Regnault upon the compressibility of gases, we have been able to determine these quantities for sulphur dioxide and ammonia and prepare tables giving results for every five degrees from  $-30^\circ$  to  $+40^\circ$ .

The method of calculation of these tables will be found in a note at the end of this essay.

For sulphur dioxide we find,

|                            |                             |
|----------------------------|-----------------------------|
| $t_2 = -15$ or $T_2 = 258$ | $t'_1 = +18$ or $T_2 = 291$ |
| $r_2 = 95.015$             | $r'_1 = 87.23$              |
| $AP_2 u_2 = 7.932$         | $AP_1 u'_1 = 8.568$         |
| $q_2 = -5.4615$            | $q'_1 = 6.554$              |
| $u_2 = 0.419$              | $u'_1 = 0.1165$             |

The table of § 22 gives  $P_1=8265$  and  $P_2=31170$ .

Making the calculations indicated by the equations (77) and (80) we find

$$x'_1=93.29 \text{ per cent.}$$

$$x_2=11.90 \text{ per cent.}$$

Equation (75) gives

$$m=2.554 \text{ kilograms.}$$

Equations (76) and (79) give

$$AW_r=27.08 \text{ whence } W_r=11.482 \text{ k'g'm.}$$

$$AW_m=1.82 \text{ whence } W_m=772 \text{ k'g'm.}$$

Finally equations (78) and (81) give

$$Q_1=222.77$$

$$Q=197.56$$

Thus the volume described by the piston of the compression cylinder being one cubic meter, 2<sup>k</sup>.554 of sulphur dioxide working between  $-15^\circ$  and  $+18^\circ$  produce 197.50 negative calories. To effect this it is necessary to introduce into the compressor cylinder at each stroke a mixture of liquid and gas of which the proportion should be 93.29 per cent. of gas and 6.71 per cent. of liquid.



. We have for ammonia

|                     |                       |
|---------------------|-----------------------|
| $t_2 = -15^\circ$   | $t'_1 = +18^\circ$    |
| $P_2 = 23669$       | $P'_1 = 82183$        |
| $r_2 = 322.53$      | $r'_1 = 301.70$       |
| $AP_2 u_2 = 28.604$ | $AP'_1 u'_1 = 31.431$ |
| $u_2 = 0.512$       | $u'_1 = 0.1621$       |
| $q_2 = -14.68$      | $q'_1 = 18.696$       |

The mean specific heat of the liquid at  $0^\circ$ ,  $c = 1.0058$ .

By means of these given values we find

|                          |                              |
|--------------------------|------------------------------|
| $x'_2 = 92.62$ per cent. |                              |
| $x'_1 = 9.68$ per cent.  |                              |
| $m = 2^k .1034$          |                              |
| $AW_r = 76.55$           | $W_r = 32,457 \text{ k'g'm}$ |
| $AW_m = 4.52$            | $W_m = 1,917 \text{ k'g'm}$  |
| $Q_1 = 634.59$           |                              |
| $Q = 562.56$             |                              |

$2^k .1034$  of ammonia working between the same limits of  $+18^\circ$  and  $-1^\circ$  and with the same dimensions of compressor cylinder as before furnish 562.56 negative calories per hour.

We will now consider ether. The vapor of ether, unlike steam, superheats

during expansion and condenses during compression. An ether machine ought, therefore, to work so that only vapor is introduced into the compressor cylinder, and not a mixture of liquid and vapor. At the end of the compression a part of the vapor becomes condensed.

We shall then have  $x'_2=1$  and the equations above found become:

$$V'_1 = mx'_1 \left( u'_1 + \frac{0,001}{\delta} \right),$$

$$V'_2 = m \left( u_2 + \frac{0,001}{\delta} \right),$$

$$\frac{x'_1 r'_2}{T_2} = \frac{r_2}{T_2} - c \cdot l \frac{T'_1}{T_2},$$

$$\frac{x_2 r_2}{T_2} = cl \frac{T'_1}{T_2},$$

$$Q_1 = mx'_1 r'_1,$$

$$Q = m(1-x_2)r_2,$$

$$AW_r = m(q'_1 - q_2 + x'_1 r'_1 - r_2),$$

$$AW_m = m(q'_1 - q_2 - x_2 r_2).$$

The empirical formulas established by Regnault for the vapor of ether are:

$$r = 94,00 - 0,0790t - 0,0008514t^2,$$

$$APu = 7,46 + 0,02747t - 0,001354t^2,$$

$$q = 0,52901t + 0,0002959t^2.$$

and we deduce:

|     |                     |     |                     |
|-----|---------------------|-----|---------------------|
| for | $t = -15$           | and | $t = +18,$          |
|     | $P_2 = 1194$ kilog. |     | $P_1 = 5456,$       |
|     | $r_2 = 94963,$      |     | $r_1 = 92,302,$     |
|     | $AP_2 u_2 = 7,014,$ |     | $AP_1 u_1 = 7,516,$ |
|     | $u_2 = 2,491,$      |     |                     |
|     | $q_2 = -7.868,$     |     | $q_1 = 9,618,$      |
|     |                     |     | $c = 0,5299,$       |

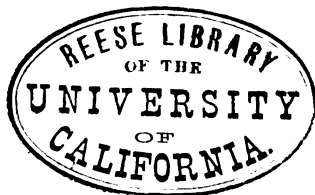
and we have  $\delta = 0,736.$

Performing the calculations indicated, we find,

$$\begin{aligned} x_2 &= 17.35, \\ x'_2 &= 100, \\ x'_1 &= 95.64, \\ m &= 0.401, \\ Q_1 &= 35^\circ.40, \\ Q &= 31^\circ.38, \end{aligned}$$

$$AW_r = 4.44,$$

$$AW_m = 0.42,$$



$$W_r = 1882 \text{kgm.}$$

$$W_m = 178 \text{kgm.}$$

The same machine working between  $-15^\circ$  and  $+18^\circ$ , will give per cubic meter of—

|                  |        |                    |
|------------------|--------|--------------------|
| Ammonia. . . . . | 562.56 | negative calories. |
| Sulphur dioxide. | 197.56 | “                  |
| Sulphuric ether. | 31.38  | “                  |

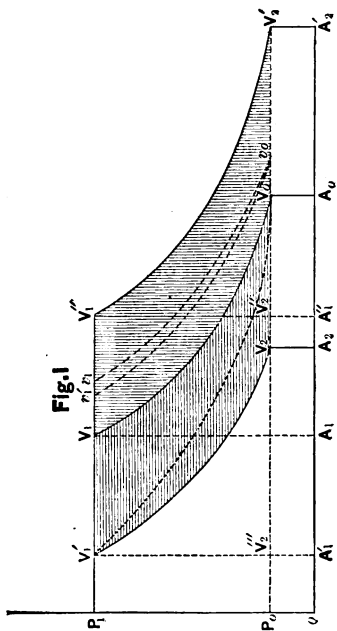
The efficiency would be 0°,0184 per kilogrammeter.

§ 25. We remark here that the positive work  $W_m$  is always small compared with the negative work  $W_r$ .

We can then without great loss of power simplify the machine by suppressing the expansion cylinder and replacing it by a simple cock so regulated as to deliver into the cooler a quantity of liquid precisely equal to the amount admitted to the compressor to obtain the determined cooling effect.

The cycle of operations is not reversible. We shall have  $\frac{Q}{AW_r} = \frac{Q}{Q_1 - Q}$ , but the proportion  $\frac{Q}{Q_1 - Q}$  will be less than  $\frac{T_1}{T'_1 - T_2}$ , and the efficiency would be less.

This manner of working is represented in the diagram, Fig. 1, by replacing the adiabatic line  $V'_1V_2$  by the two right lines  $V'_1V'''_2$  and  $V'''_2V''_2$  situated to the right of the point  $V_2$ . The quantity  $Q$  proportioned to  $V''_2V_0$  is less than the



quantity  $Q$  of the preceding case which was proportioned to  $V_2'V_0$ , and the quantity  $Q_1 - Q$  will be augmented by a quantity proportional to the area  $V_1'V'''_2V_2$ .

The equations (76), (77) and (78) remain unchanged.

The weight  $m$  of the liquid under the pressure  $P_1$  and the temperature  $T_1'$ , passing suddenly into the refrigerator, a part of the liquid is vaporized; the temperature of the mixture becomes  $T_2$  and the pressure  $P_2$ . The quantity  $x_2$  of liquid, which is vaporized, is given by the equation

$$m(q_2 - q'_1 + x_2\rho_2) + AP_2V'_2 - A(P_1 - P_2) \frac{0.001.m}{\delta} = 0,$$

which shows that the variation of internal heat  $m(q_2 - q'_1 + x_2\rho_2)$  is equal to the exterior work accomplished;

$$-AP_2V'_2 + A(P_1 - P_2) \frac{0.001.m}{\delta};$$

$V'_2$  being the volume occupied by the weight  $mx_2$  of vapor after the passage of the mixture into the refrigerant.

We have  $V'_2 = mx_2 \left( u_2 + \frac{0.001}{\delta} \right)$ .

If we neglect the very small quantity

$$AP_1 \frac{0.001 m}{\delta}$$

the preceding equation becomes:

$$x_2 r = q'_1 - q_2 \quad (84)$$

The quantity  $Q$  is again given by the equation

$$Q = m(x'_2 - x_2)r_2$$

or by reason of eq. (76)

$$Q = mr'_1 - AW_r = Q_1 - AW_r$$

from whence the performance

$$\frac{Q}{W_r} = A \frac{Q}{Q_1 - Q} \quad (85)$$

The efficiency will be less. It is easy to show that the value of  $x_2$  given by eq. (84) is always greater than that given by eq. (80). Consequently the value of  $Q$  will be less in the second case than in the first, and the ratio  $\frac{Q}{Q_1 - Q}$  will also be less.

In applying equations (84) and (85) to the same cases as those of § 24, we find for sulphur dioxide

$$x_2 = 12.64 \text{ per cent.}$$

$$Q = 195.71$$

and the performance =  $0.^\circ 0170$  per kilogrammeter. For ammonia :

$$x_2 = 10.35 \text{ per cent.}$$

$$Q = 558.11$$

and the efficiency  $0.^\circ 0172$ .

Finally for sulphuric ether

$$x_2 = 18.46 \text{ per cent.}$$

$$Q = 30.96$$

$$\text{efficiency} = 0.^\circ 0164$$

§ 26. In order to realize, either the cycle of Carnot or the non-reversible cycle indicated above, it is necessary, when we employ a liquefiable gas which superheats under compression, to introduce into the compressor cylinder at each aspiration, a mixture of liquid and vapor in such proportions that it shall all be in the state of gas at the end of the compression.

We can devise no practical means of realizing this condition. So we content ourselves when employing freezing machines that use a liquefiable gas, with



introducing into the compressor the gas without any mixture of liquid. It happens then with sulphur dioxide and ammonia that the gas superheats during compression, and therefore that during a part of the operation the machine acts like the air machine.

It is clear that under these conditions we augment the range of temperature between  $T_1$  of the gas arriving in the condenser, and  $T_2$  of the refrigerant, and consequently of the useful effect of the apparatus.

Referring again to Fig. 1 we see that we start with a volume  $v_0$  greater than  $V_0$  of the preceding case, compress the vapor to the volume  $v_1$  following the adiabatic curve  $v_0v_1$  of the superheated gas; cool it from the temperature  $T_1$  to the temperature  $T_1'$  corresponding to its liquefaction under the pressure  $P_1$ . It is then passed into the refrigerant either producing work and describing the adiabatic curve  $V_1V_2$  or by means of a cock by which means it describes the lines  $V_1'V_2'''$  and  $V_2'''V_2''$ .

The quantity of negative heat gained

by superheating is represented by the length  $V_0v_0$  and the increase of resistant work by the area  $V_0V_1v_1v_0$ .

Tracing from the point  $v_0$  the adiabatic curve of the saturated vapor, the point  $v_1'$  will be to the left of  $v_1$ .

If the compressed vapor follows the adiabatic  $v_0v_1'$ , the performance  $\frac{Q'}{Q_1' - Q}$  will be equal to the performance  $\frac{Q}{Q_1 - Q}$  of the cycle  $V_0V_1V_1'V_0$ .

But as the compression follows the line  $v_0v_1$  we see that for the same quantity  $Q'$  of obtainable negative heat, the quantity  $Q_1 - Q$  would be greater than a quantity proportional to the area  $v_0vv_1'$ .

We can say, then, that *a priori*, the theoretic efficiency of freezing machines working so as to superheat the gas is less than that of machines that work without superheating.

The difference is small as we shall see later.

§ 27. We will now examine the conditions of working of a machine, under the

supposition that we introduce into the cylinder during aspiration only gas, and in such condition as to superheat during compression.

A certain volume  $V_2$  of gas under pressure  $P_2$  and temperature  $T_2$ , it is required to find its volume  $V_1$  and its temperature  $T_1$  when it shall have attained the pressure  $P_1$  of the condenser.

If liquefiable gases behaved as do permanent gases, it would suffice to use the equations (1) to (6), which were established in § 10 for the compression of air.

But the researches of Regnault on the compressibility of gases, have established the fact that when near the liquefying point these bodies are far from following the laws of Mariotte and Gay Lussac upon which the formulas which we have used were founded.

Zeuner has given (*Théorie Mécanique de la Chaleur*) the result of his researches upon superheated steam.

He found the following relation to exist between the pressure  $P$ , the volume of the unit of weight (specific volume)  $v$ , and the absolute temperature  $T$ ,

$$P_v = BT - CP^n \quad (86)$$

in which  $C$  and  $n$  are constants to be determined by experiment

$$B = \frac{C_p n}{A} \quad (87)$$

$C_p$  being the specific heat of the vapor under constant pressure, which is constant according to Regnault.

If we make  $k = \frac{4}{3}$ ,  $B = 50.933$  and  $C = 192.50$ , we find that this formula furnishes for the specific volume of steam, numbers which agree remarkably well with the results of experiment.

Zeuner does not offer this relation as rigorously exact, but as giving much better results than the formula,

$Pv = RT$  which applies to permanent gases.

Liquefiable gases being nothing but superheated vapors, we will employ equation (84) established for superheated steam, but will determine the constants in each case employing the results of Regnault's experiments upon the dilatation and compression of gases.

If we call  $\alpha$  the coefficient of dilatation of the gas under atmospheric pressure, it is easy to see that eq. (86) gives:

$$\alpha = \frac{1}{273 - \frac{C}{B} \cdot 10.334^n}$$

$$\text{and } 10.334v_0 = 273B - C \cdot 10.334^n, \quad (88)$$

$$\text{whence } 10.334v_0\alpha = B. \quad (89)$$

an equation which gives  $B$  when we know the coefficient of dilatation and specific volume  $v_0$  at  $0^\circ$  and atmospheric pressure.

If the relation (87) were exact, it would suffice with equations (88) and (89) for determining  $B$ ,  $C$  and  $n$ . But the numbers thus obtained do not coincide, at least in the case of sulphur dioxide and ammonia with the results obtained by Regnault. Instead therefore of using equation (87) we will determine  $n$  by one of the results found by Regnault for the product  $PV$ .

Regnault gives values of  $PV$  for temperatures of  $1.7^\circ$  for sulphur dioxide, for  $8.1^\circ$  for ammonia and for pressures varying from 600 to 1200 and 1400 millimeters

of mercury. We can deduce from these tables the volume  $V_0$  at  $0^\circ$  and under pressure of 760 millimeters, and then calculate the weight  $m$  of the gas required in our examples. We then have

$$P \cdot V = mBT - mCP^n \quad (90)$$

which combined with equation (89) will furnish  $C$  and  $n$ .

For sulphur dioxide

$$a = 0.0039028; \quad v_0 = 0.3442$$

For  $P = 16.345 \text{ kgm.}$  and  $T = 274.7$ .

Regnault found,

$$\frac{PV}{m} = 3526.16$$

We deduce  $B = 13.882$

$$C = 3.8455$$

$$n = 0.44487$$

Introducing these constants into equation (86) we can obtain for  $Pv$  values which coincide in a satisfactory manner with Regnault's results.

These values are slightly less than Regnault's for pressures between 10.334 kg. and 16.345 kg., and a little larger for

pressures lying beyond these limits on either side.

For ammonia we unfortunately do not know the coefficient of dilatation; it was not determined by Regnault. As this gas is near its liquefying point at  $0^{\circ}$  we will assume its coefficient to be about the same as that of sulphur dioxide and cyanogen, which is 0.0039. In the absence of exact values determined by experiment it is clear that results obtained under the above assumption can be regarded as approximative only.

We have  $v_0 = 1.2977$  and Regnault's tables give:

$$\frac{PV}{m} = 13596 \text{ for } T = 281.1^{\circ} \text{ and } P = 19515 \text{ kgm.}$$

We then deduce

$$B = 52.4943, \quad C = 43.7144, \quad n = 0.32685,$$

§ 28. It remains now to find the equation of the adiabatic curve of a superheated vapor, of which the pressure, the specific volume and the temperature are related as follows:

$$pv = BT - Cp^n.$$

The fundamental equation of the mechanical theory of heat is, calling  $Q$  the quantity of heat furnished to a body,  $U$  its internal work, and supposing the external pressure is always equal to the expansive force :

$$dQ = A(dU + pdv),$$

and as  $U$  is a function of  $p$  and  $v$ , we have :

$$dQ = A \left\{ \frac{dU}{dp} dp + \left( \frac{dU}{dv} + p \right) dv \right\}.$$

Assuming  $\frac{dU}{dp} = X$   $\frac{dU}{dv} + p = Y$ ,

we have  $dQ = A (Xdp + Ydv)$  (91)

or  $dQ = AT \left( \frac{x}{T} dp + \frac{Y}{T} dv \right)$

and since  $dU$  is an exact differential,

$$\frac{dX}{dv} = \frac{dY}{dp} - 1.$$

We know that the factor  $\frac{1}{T}$  is the factor of integrability of the function  $Xdp + Ydv$ ; and we deduce



$$T = Y \frac{dt}{dp} X \frac{dt}{dv} \quad (92)$$

We also have in virtue of equation (86),

$$\frac{dt}{dp} = \frac{v}{B} + \frac{nCp^{n-1}}{B}$$

and 
$$\frac{dt}{dv} = \frac{p}{B}.$$

If we suppose that the pressure remain constant,  $dp=0$ , and eq. (91) gives

$$dQ_p = AYdv.$$

But,  $dQ_p = c_p dt$ , calling  $c_p$  the specific heat at constant pressure, which we suppose constant and which is known. We have then :

$$Y = \frac{c_p}{A} \frac{dt}{dv} = \frac{c_p}{A}$$

and from eq. (92),

$$X = -\frac{BT}{p} + \frac{c_p}{AB}(v + nCp^{n-1})$$

and finally,

$$dQ = A$$

$$\left\{ \frac{c_p}{AB} (p dv + v dp) - v dp + \left( \frac{n c_p}{AB} - 1 \right) C p^{n-1} dp \right\} \quad (93)$$

For the equation of an adiabatic curve, it is necessary to make  $dQ=0$ . We have then :

$$\left(\frac{c_p}{AB}-1\right)dpv + p dv + \left(\frac{nc_p}{AB}-1\right)Cp^{n-1}dp=0. \quad (94)$$

Introducing the value of T from equation (86), it becomes.

$$\frac{c_p}{AB}-\frac{dt}{T}=\frac{dp}{p} \text{ and integrating } \frac{c_p}{AB} \ln T = \ln p + \text{const.}$$

or finally

$$\left(\frac{T}{T_0}\right)^{\frac{c_p}{AB}} = \frac{p}{p_0}, \quad (95)$$

an equation analogous to equation (4) , which we found for air.

Replacing T by this value in equation (86) we get finally for the equation of the adiabatic curve

$$pv = BT_0 \left(\frac{p}{p_0}\right)^{\frac{AB}{c_p}} - Cp^n. \quad (96)$$

If  $\frac{AB}{c_p}$  be equal to  $n$ , as Zeuner admits, for superheated steam, this equation be-

comes  $pv_k = \text{a constant}$ , and it is similar to that which represents the adiabatic curve of the permanent gases.

Eq. (94) gives the work of compression

$$pdv = -dW \left(1 - \frac{c_p}{AB}\right) dpv + \left(1 - \frac{nc_p}{AB}\right) Cp^{n-1} dp$$

whence

$$W = \left(\frac{c_p}{AB} - 1\right)(pv - p_0 v_0) + \left(\frac{c_p}{AB} - \frac{n}{1}\right) C(p^n - p_0^n) \quad (97)$$

or again

$$W = \left(\frac{c_p}{AB} - 1\right) B(T - T_0) + C \left(1 - \frac{1}{n}\right) (p^n - p_0^n) \quad (98)$$

and

$$W = \left(\frac{c_p}{AB} - 1\right) B(T - T_0) + C \frac{1 - \frac{1}{n}}{p_0^n} \left\{ \left(\frac{T}{T_0}\right)^{\frac{nc_p}{AB}} - 1 \right\} \quad (99)$$

§ 29. We can now establish the equations relating to the compression of a liquefiable gas in a cylinder. A weight  $m$  of gas occupying the volume  $V_1$  at the temperature  $T_1$ , and under the pressure  $P_1$  is compressed until the pressure is  $P_2$  of the condenser. The temperature  $T_2$

at the end of the compression will be given by the equation (95).

$$T_1 = T_2 \left( \frac{P_1}{P_2} \right)^{\frac{AB}{c_p}} \quad (100)$$

and the work of compression including the flowing of the the gas is

$$\left. \begin{aligned} W_r &= \frac{mc_p}{AB} (P_1 V_1 - P_2 V_2) + m \left( \frac{AB}{c_p} - \frac{1}{n} \right) \\ &\quad C(P_1^n - P_2^n) \\ \text{or} \\ W_r &= \frac{mc_p}{A} (T_1 - T_2) - \frac{mc P_2^n}{n} \left\{ \left( \frac{T_1}{T_2} \right)^{\frac{nc_p}{AB}} - 1 \right\} \end{aligned} \right\} \quad (101)$$

$m$  is given by the equation

$$= \frac{P_2 V_2}{BT_2 - CP_2^n} = \frac{V_2}{u_2 + \frac{0.001}{\delta}} \quad (102)$$

the final volume

$$V_1 = V_2 \frac{P_2}{P_1} \frac{BT_1 - CP_1^n}{BT_2 - CP_2^n}$$

We cool the gas in the condenser under constant pressure. The volume  $V_1$  becomes  $V_1'$  at the moment the temperature becomes  $T_1'$ ; since the gas is liquefied we have;

$$V_1' = V_2 \frac{P_2}{P_1} \cdot \frac{BT_1' - CP_1^n}{BT_2 - CP_2^n}$$

and the quantity of heat removed from the condenser is:

$$Q_1 = mc_p (T_1 - T_1') + mr_1' \quad (103)$$

The volume occupied by the liquid is

$$v_1 = \frac{0.001 \cdot m}{\delta}$$

$\delta$  being the density of the liquid supposed constant.

The liquid is then passed into the refrigerant without producing work.

The quantity  $mx_2$  of gas which vaporizes while the pressure passes from  $P_1$  to  $P_2$  and the temperature from  $T_1'$  to  $T_2$  is by equation (84);

$$mx_2 r_2 = m(q_1' - q_2).$$

The quantity of negative heat obtained is:

$$\begin{aligned} Q &= m(1 - x_2)r_2 \\ \text{or} \quad Q &= m(\lambda_2 - q_1') \end{aligned} \quad (104)$$

and we have

$$\begin{aligned} Q_1 - Q &= mc_p (T_1 - T_1') + m(r_1' + q_1' - r_2 - q_2) \\ \text{or} \quad Q_1 - Q &= mc_p (T_1 - T_1') + m(\lambda_1' - \lambda_2) \end{aligned}$$

We can verify the equality  $Q_1 - Q = AW$ ,  
or

$$\lambda_1' - \lambda_2 = c_p(T_1' - T_2) - \frac{AC}{n}(P_1^n - P_2^n)$$

Referring to the fundamental equation

$$dQ = AdU + APdv$$

and making  $dQ = 0$  it becomes

$$mdU = -mPdv = -dW.$$

and consequently

$$U_1 - U_2 = \left(\frac{C_p}{AB} - 1\right)B(T_1 - T_2) + C\left(1 - \frac{1}{n}\right)(P_1^n - P_2^n) \quad (105)$$

We have furthermore by definition,

$$\lambda = AU + APv,$$

an equation which signifies that the total heat of the vapor at  $t^\circ$  is equal to the internal heat  $AU$  augmented by the thermal equivalent of the work of vaporization and dilatation.

We have then

$$\lambda_1 - \lambda_2 = C_p(T_1 - T_2) - \frac{AC}{n}(P_1^n - P_2^n)$$

This equation is applicable to a superheated vapor above its point of saturation.

It applies also at the point of saturation; we have then

$$\lambda_1' - \lambda_2 = C_p (T_1' - T_2) - \frac{AC}{n} (P_1^n - P_2^n) \quad (106)$$

which verifies the equation

$$Q_1 - Q = A W_r.$$

Equation (105) can be written :

$$U - U_0 = \left( \frac{C_p}{AB-1} \right) (Pv - P_0 v_0) + \left( \frac{C_p}{AB} - \frac{1}{n} \right) C(P^n - P_0^n)$$

$$\text{If we make } \frac{C_p}{AB} - \frac{1}{n} = 0.$$

the equation becomes

$$U = U_0 + \frac{1-n}{n} (Pv - P_0 v_0)$$

Under this form it expresses Hirn's law of superheated vapors, and may be thus expressed:—from the point of condensation, to the point at which the superheated vapor possesses the same properties as the permanent gases, the product  $p v$  remains constant while the internal work remains the same.

But the equation

$$\frac{c_p}{AB} = \frac{1}{n}$$

is not verified for the cases of the two liquefiable gases which we have studied, and consequently we cannot apply to them the law of Hirn.

§ 30. We will now take a numerical example and suppose as in the preceding case, that a cubic meter of gas is admitted at the temperature of  $-15^\circ$  under a pressure corresponding to this temperature, and that it is compressed until its tension is that of the condenser and that the temperature of this latter is, in the interior,  $+18^\circ$ .

*Sulphur dioxide.* Equation (102) gives

$$m = \frac{1}{0.419 + \frac{0.001}{1.42}} = 2^k.382$$

Equation (100) gives; making

$$c_p = 0.15438$$

after Regnault, and

$$\frac{AB}{c_p} = 0.211882;$$

$$T_1 = T_2 \left( \frac{P_1}{P_2} \right)^{0.211882} = 334.31 \quad \text{or} \quad t_1 = 68^\circ.80$$



Equations (103) and (104) give

$$Q_1 = 227.49$$

$$Q = 197.75$$

whence  $AW_r = Q_1 - Q = 28.71$

and  $W_r = 121.75$

and the theoretic performance = 0.0162 or 4.374 calories per horse power per hour.

In a double acting engine working at high velocity we estimate the resistances at about 15 per cent. of the power expended.

$1.15W_r = 13.998$  and the performance becomes 0.0141 or 3.807 calories per horse power, per hour.

This performance is double that of the machine working with dry air between the same limits of temperature. This difference shows not that the air is theoretically a less efficient agent in the production of cold, but that to produce the same useful effect, the air machine having much larger dimensions than the liquefiable gas machines will experience proportionally greater loss through resistances.

§ 31. Generally with sulphur dioxide



we do not get as low a temperature as  $-15^{\circ}$ .

The opening of the cock which leads from the condenser to the cooler is so regulated that the pressure in the latter is about  $\frac{9}{10}$  of an atmosphere, which corresponds to a temperature of  $-12^{\circ}.41$ .

$$P_2 = 9301 \text{ kg. } t_2 = -12^{\circ}.41.$$

With these values the tables, given at the end of this memoir, give

$$m = \frac{1}{v_2} = 2^k.784$$

$$r_2 = 94.377$$

$$q_2 = -4.517$$

$$u_2 = 0.3863$$

and by means of equations (100), (102), (103) and (104) of § 29 it is easy to calculate  $T_1$ ,  $Q_1$ ,  $Q$  and  $W_r$ .

The results of these calculations are recorded in the following table, which gives the negative heat obtained, the work absorbed and the performance per cubic meter of sulphur dioxide, supposing the apparatus regulated for a temperature of  $-12^{\circ}.41$  in the refrigerant, and that the temperature of the interior of the condenser varies from  $+15^{\circ}$  to  $+40^{\circ}$ :

| Temperature of<br>condenser, inside. | Pressure corresponding<br>$P_1$ | Temperature after<br>compression, $t_1$ . | Heat absorbed by<br>water of the<br>condenser. | Negative heat. | Theoretical work<br>of compression. | Work including<br>passive resistances. | Negative calories developed.    |                                           |                                 |                                           |
|--------------------------------------|---------------------------------|-------------------------------------------|------------------------------------------------|----------------|-------------------------------------|----------------------------------------|---------------------------------|-------------------------------------------|---------------------------------|-------------------------------------------|
| degrees                              | kilog.                          | degrees                                   | cal.                                           | cal.           | kgm.                                | kgm.                                   | Per theoretic<br>kilogrammeter. | Per theoretic<br>horse power<br>per hour. | Per effective<br>kilogrammeter. | Per effective<br>horse power<br>per hour. |
| 15                                   | 28,074                          | 56.20                                     | 243.35                                         | 218.09         | 10,735                              | 12,335                                 | 0.02031                         | 5.484                                     | 0.01768                         | 4.774                                     |
| 20                                   | 33,474                          | 68.69                                     | 243.19                                         | 213.38         | 12,444                              | 14,310                                 | 0.01715                         | 4.630                                     | 0.01491                         | 4.026                                     |
| 25                                   | 39,645                          | 81.15                                     | 243.04                                         | 208.66         | 14,609                              | 16,890                                 | 0.01428                         | 3.856                                     | 0.01242                         | 3.353                                     |
| 30                                   | 46,659                          | 93.56                                     | 242.80                                         | 203.94         | 16,515                              | 19,022                                 | 0.01235                         | 3.334                                     | 0.01072                         | 2.894                                     |
| 35                                   | 54,585                          | 105.93                                    | 242.56                                         | 199.21         | 18,425                              | 21,189                                 | 0.01081                         | 2.919                                     | 0.00940                         | 2.538                                     |
| 40                                   | 63,496                          | 118.26                                    | 242.27                                         | 194.48         | 20,312                              | 23,359                                 | 0.00957                         | 2.584                                     | 0.00832                         | 2.246                                     |

We see that the performance diminishes more than one-half when the temperature of the interior of the condenser rises from  $15^{\circ}$  to  $40^{\circ}$ .

The figures of the last column do not nearly represent the number of calories really produced and utilized. It is necessary to take into account the loss occasioned by the pipes; the waste spaces in the cylinder; of loss of time in opening of the valves; of the leakage around the piston and valves; of the reheating by the external air; and finally, when ice is being made, of the quantity of the ice melted in removing the blocks from their molds.

It requires about 100 calories to congeal to  $-7^{\circ}$  a kilogram of water taken at  $15^{\circ}$  or  $16^{\circ}$ . Manufacturers estimate that practically the sulphur dioxide apparatus using water at  $12^{\circ}$  or  $13^{\circ}$ , produces 25 kilograms of ice, or 2,500 calories per horse power per hour, measured on the driving shaft, which is about 55 per cent. of the theoretic efficiency indicated above.

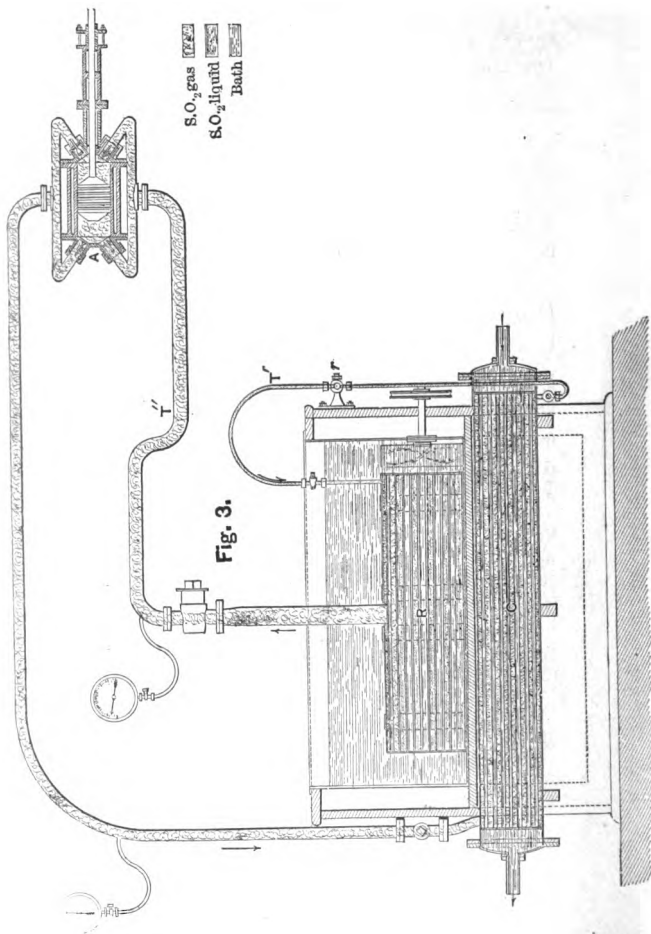
Fig. 3 represents the Pictet machine from a design furnished us by the inventor. It has a double-acting compression cylinder with four valves. The cylinder is furnished with a jacket, within which a current of cold water is made to circulate.

The gas is compressed to a tension corresponding to the temperature of the water employed for cooling, generally 1.8 to 2 kilograms effective pressure; then it is discharged by the pipe T into the condenser C where it is liquefied.

This condenser is like the surface condensers of marine engines. It has a surface of about 24 square meters for 100,000 *theoretic* calories per hour, or 48 square meters for 100,000 *effective* calories per hour measured by the ice produced.

The quantity of water employed depends upon the difference of temperature to be allowed between the inside and outside of the condenser.

If this difference is to be 5° each litre of water releases 5 calories and the



quantity of water to be employed will be for 100 theoretic calories produced

$$\frac{Q_1 100}{5Q} = 20 \frac{Q_1}{Q}$$

which would require for the example of § 31 and for a temperature of 20° in the condenser, 22.8 litres.

The liquid dioxide passes into the refrigerant R by the pipe T', the supply being regulated by the cock *r* so that the pressure shall be  $\frac{2}{10}$  of an atmosphere in the refrigerant and 3 atmospheres in the condenser. If the outlet by the cock be diminished the pressure is lowered in the cooler, and the temperature is also lowered, but the useful effect also diminishes, since for the same volume described by the compressor piston, less weight of gas is used. We have in this machine, therefore, the same facilities for varying the useful effect as in the air machines.

The refrigerant is constructed like the condenser. Its surface is 29 square meters for each 100,000 theoretic negative calories produced per hour. It is

immersed in an incongealable bath formed of a solution of calcium chloride.

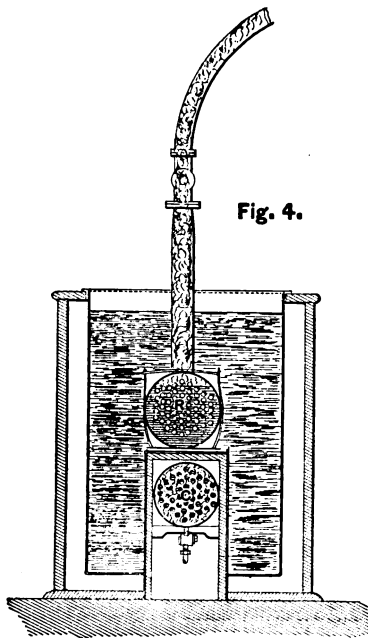
The temperature of the interior of the refrigerant being  $-12^{\circ}$ , that of the bath being  $-7^{\circ}$ . In this bath are immersed the tanks or moulds within which the water is frozen.

Finally the sulphur dioxide returns to the compressor cylinder by the pipe T'.

The dioxide may be employed continuously so long as no air is permitted to enter the joints. Any leakage might lead to the production of the trioxide and possibly sulphuric acid which would lead to injury to machine. Exceptional care is required in maintaining tight joints.

Some experiments with an ammonia machine have not yielded very good results; but the want of success seems to have resulted rather from an imperfect action of the surface of the refrigerant than from any inherent defect in the gas itself. Ammonia gas prevents the advantage of affording about three times the useful effect as sulphur dioxide for the same volume described by the piston.





But this advantage is balanced by the inconvenience of higher pressures and consequently more leakage, &c.

Between the limits of temperature of  $12^{\circ}.41$  in the refrigerant and  $+ 18^{\circ}$  in the condenser we find for ammonia :

$$P_2 = 26559 \text{ kilos.}$$

$$r_2 = 321.06$$

$$u_2 = 0.461$$

$$q_2 = -1219$$

and we have  $C_p = 0.50836$

$$\frac{AB}{C_p} = 0.242615.$$

We deduce for each cubic meter described by the piston:

$$m = 2.163 \text{ k.}$$

$$T_1 = 342.75 \quad t_1 = 69^\circ.75$$

$$Q_1 = 709.48$$

$$Q = 627.03$$

$$AW_r = Q_1 - Q = 82.45 \quad W_r = 34.959 \text{ kg.}$$

Theoretic efficiency: 0.0179 or 4.833 per horse power per hour.

Working the apparatus between  $-30^\circ$  and  $+18^\circ$  we find.

$$P_2 = 11918k$$

$$r_2 = 330.48$$

$$u_2 = 0.9463$$

$$q_2 = -31.82$$

$$m = 1.0553k$$

$$T_1 = 388.20$$

$$t_1 = 115.20$$

$$Q_1 = 370.52$$

$$Q = 295.44$$

$$AW_r = Q_1 - Q = 75.08 \qquad W_r = 31.834$$

Theoretic result: 0.00928 or 2505 per horse power per hour.

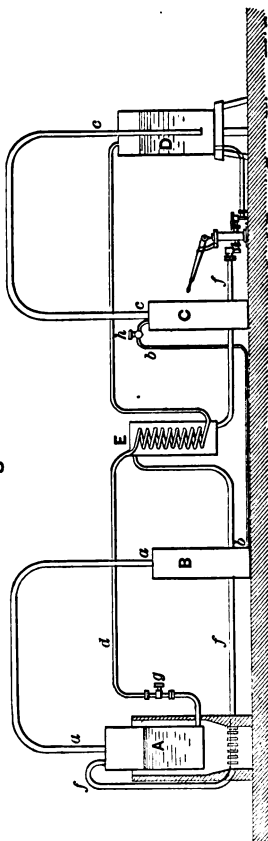
## CHAPTER IV.

### MACHINES EMPLOYING CHEMICAL ACTION.

§ 34. It remains to discuss the ice making machines which employ chemical affinity in their mode of action, and of which the ammonia machine of M. Carré is the type.

Fig. 5 exhibits the disposition of the parts of this apparatus. It consists of a boiler A which contains a concentrated solution of ammonia in water; this boiler is heated either directly by a fire as shown in the figure, or indirectly by pipes leading from a steam boiler. The condenser B communicates with the upper part of the boiler by the tube *aa*; it is cooled externally by a current of cold water. The *réfrigérant* C is so constructed as to utilize the cold produced; the upper part of it is in communication with the lower part of the condenser by

Fig. 5.



means of the tube *bb*. The details of the construction are not shown in the figure. An absorption chamber D is filled with a weak solution of ammonia; the tube *cc* puts this chamber in communication with the refrigerant C.

The absorption chamber communicates with the boiler by two tubes. One *dd*, leads from the bottom of the boiler to the top of the chamber D; the other, *ff*, leads from the bottom of D to the top of the boiler. Upon the pipes *ff* is mounted a little pump whose use is to force the liquid from the absorption chamber where the pressure is maintained at about one atmosphere, into the boiler, where the pressure is from 8 to 12 atmospheres.

The change of temperature is managed through the attachments to the pipes *ff* and *dd* in a manner that will be easily comprehended by an inspection of the figure.

To work the apparatus the ammonia solution in the boiler is first heated. This releases the gas from the solution

and the pressure rises. When it reaches the tension of the saturated gas at the temperature of the condenser, there is a liquefaction of the gas, and also of a small amount of steam. By means of the cock *h*, the flow of the liquefied gas into the refrigerant C is regulated. It is here vaporized by absorbing the heat from the substance placed here to be cooled. As fast as it is vaporized it is absorbed by the weak solution in D. The small quantity of watery vapor is carried along mechanically.

Under the influence of the heat in the boiler A, the solution is unequally saturated, the stronger solution being uppermost.

The weaker portion is conveyed by the pipe *dd* into the chamber D, the flow being regulated by the cock *g*, while the pump sends an equal quantity of strong solution from D back to the boiler. While these exchanges are brought about in the solutions, there is also an exchange of temperatures whereby the weak liquid arrives cold in the absorp-

tion chamber, and the strong solution is delivered in the boiler hot.

The working of the apparatus depends upon the adjustment and regulation of the cocks *g* and *h*, and of the pump; by means of these, the pressure is varied, and consequently the temperature in the refrigerant C controlled.

It is seen that the working is similar to that of the machines described in the preceding chapters. The chamber D fills the office of aspirator, and the boiler A plays the part of compressor.

The mechanical force producing exhaustion, is here replaced by the affinity of water for ammonia gas; and the mechanical force required for compression is replaced by the heat which severs this affinity and sets the gas at liberty. We see then in advance that we shall again find a greater part of the equations already established in the discussion of the liquefiable gas machines.

§ 35. We will assume at first, that under the influence of the heat applied to the boiler, ammonia gas only is driven

off, and no steam. We will assume a certain weight of the gas to enter the boiler in a state of solution; being heated, it will be separated from the water, requiring a certain quantity of heat which we will call  $Q'$ . Then, being conducted to the condenser, it will be cooled and then liquefied, and will impart to the water surrounding the coils a quantity of heat  $Q_1$ . In the refrigerant it is evaporated, borrowing from the exterior a quantity of heat  $Q$ ; it is next absorbed by the liquid in the chamber D, disengaging a certain amount of heat to the liquid (which may be deducted from the total amount required in the boiler); and, finally, it is reconveyed to the boiler, where it arrives in its original condition. By reason of the exchange of temperature effected at E, all the heat of the weak solution going out of the boiler, is restored to the strong solution entering it, so that the changes of temperature in the water are effected without expenditure of heat.

In the complete cycle if we neglect the



small amount of work performed by the pump, and the heating and cooling due to contact with the air, it is clear that all the heat from external sources, being  $Q'$  from the boiler, and  $Q$  from the refrigerant, will be equal to the amount  $Q_1$  carried away by the water of the condenser.

We have then

$$Q' = Q_1 - Q \quad \text{and the}$$

efficiency will be expressed by

$$\frac{Q}{Q_1 - Q} \quad \text{which is identical}$$

with that found for the machines depending on mechanical action.

$Q'$  the quantity of heat which it is necessary to expend in order to produce the quantity  $Q$  of negative calories, being equal to  $Q_1 - Q$ , has the same value as the quantity  $AW_r$ , the calorific equivalent of the mechanical work expended in the machines previously discussed, to produce this same quantity  $Q$  of negative calories. We proceed to show that between the same limits of temperature in

the condenser and refrigerant, and for the same value of  $Q$ , the quantity  $Q'$  in this class of machines, is equal, very approximately at least, to the quantity  $AW_r$ .

We arrive then at this remarkable result; that in all the ice machines, when they work between the same limits of temperature, the theoretic quantity of negative heat produced is exactly the same for each calorie expended, whether it is directly produced by chemical action, or indirectly under the form of mechanical work.

But as a calorie represented by 424 kilogrammeters costs in the best heat motors an expenditure of at least 10 calories in the fire, it would seem that the chemical machines possess a considerable advantage over all the others, since in these latter the heat is employed directly, and not under the expensive form of mechanical work. Practically, however, this advantage is much less than that which seems to result from the above calculations; as we will proceed to show.

§ 36. We will assume the hypothesis mentioned in the beginning of the preceding section, and determine the quantities  $Q'$ ,  $Q_1$ , and  $Q$  in terms of the temperatures, the pressures and weights of the gas employed.

We will preserve the notations of the previous chapter.  $T_1$  being the absolute temperature of the gas as it enters the condenser;  $T_1'$  its absolute temperature in the condenser, and  $T_2$  the absolute temperature in the refrigerant.

Let  $m$  be the weight of the gas considered, occupying the volume  $V_2$  at the temperature  $T_2$ , and under the pressure  $P_2$  at its entrance into the absorption chamber.

Let  $AU$  be the internal heat at the temperature  $T$ ;  $qe$  the heat necessary to raise a kilogram of water from  $0^\circ$  to  $1^\circ$ .

After the gas has been absorbed by the water, the absolute temperature of the mixture will be  $T'_2$ .

During the process of absorption of the gas, there is an amount of external work accomplished equal to  $P_2(V_2 - w)$ ,  $w$  of being the volume of water.

The difference in internal heat before and after this operation is equal to this external work. We have then

$$q_{e_1}' + mAU_1' - q_{e_2} - mAU_2 = AP_1(V_1 - w).$$

The solution is conveyed to the boiler, and there heated until all the gas is driven off. It then occupies the volume  $V_1$  under the pressure  $P_1$ , and at the temperature  $T_1$ .

The necessary quantity of heat  $Q''$  is equal to the difference in quantities of internal heat, augmented by the exterior work accomplished. This work is equal to  $P_1(V_1 - w)$  less the work of the pump,  $(P_1 - P_2)w$ .

We have then

$$Q'' = q_{e_1} - q_{e_2}' + mAU_1 - mAU_2 + AP_1(V_1 - w) - A(P_1 - P_2)w.$$

Adding this equation to the preceding, member to member, we find

$$Q'' = q_{e_1} - q_{e_2} + mA(U_1 - U_2) + AP_1V_1 - AP_2V_2$$

This equation is established without taking account of the effect of exchange of temperature. There is furnished to the

solution which enters the boiler a quantity of heat precisely equal to  $q_{e_1} - q_{e_2}$ . The quantity of heat  $Q'$  to be supplied by the boiler, in order to bring the pressure of the gas from  $P_2$  to  $P_1$ , and from the temperature  $T_2$  to  $T_1$  is then

$$Q' = mA(U_1 - U_2) + AP_1V_1 - AP_2V_2 \quad (107)$$

The equations 101 and 105 gave, in case of compression by a mechanical force,

$$AW_r = mA(U_1 - U_2) + AP_1V_1 - AP_2V_2$$

which is identical with the preceding.

We have then  $Q' = AW_r$  provided that the temperature  $T_1$  in the case where the change of pressure of the gas is obtained by the heat combined with the chemical action, is the same as in the case where the change is due to a mechanical force. Experiment proves that it is nearly so.

It appears that the temperature to which it is necessary to heat the ammonia solution to obtain a given pressure is higher as the solution becomes weak. Now in the ice machines the so-

lution conveyed to the boiler contains rather less of the gas as the pressure in the refrigerant becomes more feeble. We understand therefore how the temperature  $T_1$  ought to increase as the temperature  $T_2$  of the refrigerant diminishes. Unfortunately, precise experiments upon this point are wanting.

A series of observations made by M. Rouart upon a Carré machine is here-with given.

The first column of each table gives the absolute pressures in atmospheres and kilograms; the second the temperatures observed in the boiler; the fourth, the temperatures of water in the condenser; the fifth column gives the temperatures of the liquefied gas corresponding to the pressures in the first column (see table in § 22); the temperatures are those of the interior of the condenser, and are naturally more elevated than the exterior.

In the case of mechanical compression the final temperature  $T_1$  is related to the initial temperature and to the initial

and final pressures as expressed by the equation (100)

$$T_1 = T_2 \left( \frac{P_1}{P_2} \right)^{\frac{\Delta B}{C_p}}$$

The third column of the table gives the temperatures calculated by this formula, supposing  $T_2 = 243$  and  $P_2 = 11,918$ .

For the mean pressures the calculated temperatures coincide nearly with the observations. For the higher pressures the calculated pressures are higher than the observed. But it is necessary to remark that in this case the watery vapor mixed with the gas exerts a greater influence, and that the true gas pressures ought to be sensibly less than the pressures which have served as a basis for calculation.

The condensation in the condenser and the evaporation in the refrigerant, are brought about exactly as in the case of the machines acting by mechanical force. We shall have then, as in § 27,

$$Q_1 = mc_p (T_1 - T_1') + mr_1',$$

$$x_1 r_2 = q_1' - q_2,$$

| Pressure in Boiler. |         | Temperature of Boiler |            |
|---------------------|---------|-----------------------|------------|
| Atm.                | Kilog.  | Observed.             | Calculated |
|                     |         | Degrees.              | Degrees.   |
| 1½                  | 15,501  | 48                    | —          |
| 2                   | 20,668  | 58                    | —          |
| 2½                  | 25,835  | 65                    | —          |
| 3                   | 31,002  | 70                    | —          |
| 3½                  | 36,169  | 75                    | —          |
| 4                   | 41,336  | 80                    | —          |
| 4½                  | 46,503  | 84                    | —          |
| 5                   | 51,670  | 88                    | —          |
| 5½                  | 56,837  | 92                    | —          |
| 6                   | 62,004  | 94                    | —          |
| 6½                  | 67,171  | 100                   | —          |
| 7¼                  | 74,921  | 106                   | 106        |
| 7½                  | 77,505  | 108                   | 109        |
| 8                   | 82,672  | 112                   | 116        |
| 8½                  | 87,839  | 116                   | 121        |
| 9                   | 93,006  | 120                   | 127        |
| 9½                  | 98,173  | 124                   | 132        |
| 10                  | 103,340 | 128                   | 137        |
| 10½                 | 108,507 | 132                   | 142        |
| 11                  | 113,674 | 136                   | 147        |
| 12                  | 123,998 | 142                   | 156        |
| 13                  | 134,332 | 146                   | 164        |
| 14                  | 144,666 | 152                   | 172        |
| 15                  | 155,000 | 156                   | 180        |
| 15                  | 155,000 | 158                   | 180        |



| Temperature of water of condenser. | Temperature inside of condenser. | Difference. | Remarks.                                            |
|------------------------------------|----------------------------------|-------------|-----------------------------------------------------|
| Degrees.                           | Degrees.                         | Degrees.    |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 9                                  | —                                | —           |                                                     |
| 10                                 | —                                | —           |                                                     |
| 10                                 | 15.0                             | 5.0         | The gas liquefies and the apparatus begins to work. |
| 10                                 | 16.1                             | 6.1         |                                                     |
| 12                                 | 18.0                             | 6.0         |                                                     |
| 13                                 | 20.0                             | 7.0         |                                                     |
| 14                                 | 21.7                             | 7.7         |                                                     |
| 15                                 | 23.3                             | 8.8         |                                                     |
| 17                                 | 25.1                             | 8.1         |                                                     |
| 17                                 | 26.7                             | 9.7         |                                                     |
| 19                                 | 28.1                             | 9.1         |                                                     |
| 24                                 | 31.0                             | 7.1         |                                                     |
| 30                                 | 32.8                             | 2.8         |                                                     |
| 35                                 | 36.0                             | 1.0         |                                                     |
| 37                                 | 38.0                             | 1.0         |                                                     |
| 39                                 | 38.0                             | —           |                                                     |



| Absolute pressures. |         | Temperature of Boiler |            |
|---------------------|---------|-----------------------|------------|
| Atm.                | Kilog.  | Observed.             | Calculated |
|                     |         | Degrees.              | Degrees.   |
| 3                   | 31,002  | 73                    | —          |
| 4½                  | 46,503  | 90                    | —          |
| 5                   | 51,670  | 94                    | —          |
| 5½                  | 56,837  | 100                   | —          |
| 6                   | 62,004  | 103                   | —          |
| 6½                  | 67,171  | 106                   | —          |
| 7                   | 72,338  | 110                   | —          |
| 7½                  | 77,505  | 118                   | 109        |
| 8                   | 82,672  | 124                   | 116        |
| 8½                  | 87,839  | 130                   | 121        |
| 9                   | 93,006  | 136                   | 127        |
| 9½                  | 98,173  | 140                   | 132        |
| 10                  | 103,340 | 146                   | 137        |
| 10¾                 | 111,089 | 147                   | 145        |
| 11¾                 | 121,423 | 148                   | 153        |
| 13                  | 134,332 | 148                   | 164        |
| 14                  | 144,666 | 154                   | 172        |
| 15                  | 155,000 | 160                   | 180        |
| 15½                 | 160,167 | 163                   | 180        |

$$Q = m(1 - x_1)r_1 = mr_1 - m(q_1' - q_2),$$

$$m = \frac{V_1}{u_1 + \frac{0.001}{\delta}} = \frac{V_1}{v_1}$$

$$Q' = Q_1 - Q.$$

| Temperature of<br>condenser<br>water<br>(observed). | Temperature of<br>interior of<br>condenser<br>(calculated) | Difference of<br>tempera-<br>tures. | Observations.                   |
|-----------------------------------------------------|------------------------------------------------------------|-------------------------------------|---------------------------------|
| Degrees.                                            | Degrees.                                                   | Degrees.                            |                                 |
| 8                                                   | —                                                          | —                                   |                                 |
| 8                                                   | —                                                          | —                                   |                                 |
| 8                                                   | —                                                          | —                                   |                                 |
| 8                                                   | —                                                          | —                                   |                                 |
| 8                                                   | —                                                          | —                                   |                                 |
| 8                                                   | —                                                          | —                                   |                                 |
| 9                                                   | 14.1                                                       | —                                   | } The liquefied<br>gas appears. |
| 10                                                  | 16.1                                                       | 6.1                                 |                                 |
| 12                                                  | 18.0                                                       | 6.0                                 |                                 |
| 14.5                                                | 20.0                                                       | 5.5                                 |                                 |
| 15                                                  | 21.7                                                       | 6.7                                 |                                 |
| 16                                                  | 23.3                                                       | 7.3                                 |                                 |
| 17                                                  | 25.1                                                       | 8.1                                 |                                 |
| 19                                                  | 27.4                                                       | 8.4                                 |                                 |
| 16 (?)                                              | 30.4                                                       | 14.4 (?)                            |                                 |
| 16 (?)                                              | 32.8                                                       | 16.8 (?)                            |                                 |
| 35                                                  | 36.0                                                       | 1                                   |                                 |
| 38                                                  | 38.0                                                       | 0                                   |                                 |
| 38                                                  | 40.0                                                       | 1                                   |                                 |

The two following tables give the results of calculations for one cubic meter of ammonia gas, for temperatures in the condenser ranging from  $+15^{\circ}$  to  $+40^{\circ}$ . In the first the temperature of

the interior of the refrigerant is taken at  $-15^{\circ}$ . In the second table it is  $-30^{\circ}$ .

The numbers in the last column are calculated on the supposition that a kilogram of coal burned yields 4000 calories.

First case:  $t_2 = -15^{\circ}$ ,  $m = 1^{\text{k}}.932$ .

| Temp. interior<br>of condenser. | Temperature of<br>boiler. | Calories removed<br>by condenser. | Negative calories<br>produced. | Calories<br>expended. | Theoretic<br>performance. | Theoretic result<br>per kilogram<br>of coal. |
|---------------------------------|---------------------------|-----------------------------------|--------------------------------|-----------------------|---------------------------|----------------------------------------------|
| deg.                            | deg.                      | cal.                              | cal.                           | cal.                  | cal.                      | cal.                                         |
| 15                              | 67.77                     | 638.71                            | 564.83                         | 73.88                 | 7,645                     | 30,580                                       |
| 20                              | 81.74                     | 640.76                            | 554.49                         | 86.27                 | 6,427                     | 25,708                                       |
| 25                              | 95.69                     | 642.61                            | 543.98                         | 98.63                 | 5,515                     | 22,060                                       |
| 30                              | 109.61                    | 644.12                            | 533.29                         | 110.83                | 4,813                     | 19,252                                       |
| 35                              | 123.47                    | 645.53                            | 522.43                         | 123.10                | 4,244                     | 16,976                                       |
| 40                              | 137.27                    | 646.57                            | 511.31                         | 135.26                | 3,779                     | 15,116                                       |

Second case:  $t_1 = -30^\circ$ ,  $m = 1^k.023$ .

| Temp. interior<br>of condenser. | Temperature of<br>boiler. | Calories removed<br>by condenser. | Negative calories<br>produced. | Calories<br>expended. | Theoretic<br>performance. | Theoretic result<br>per kilogram<br>of coal. |
|---------------------------------|---------------------------|-----------------------------------|--------------------------------|-----------------------|---------------------------|----------------------------------------------|
| deg.                            | deg.                      | cal.                              | cal.                           | cal.                  | cal.                      | cal.                                         |
| 15                              | 106.07                    | 361.77                            | 293.04                         | 68.73                 | 4,263                     | 17,052                                       |
| 20                              | 121.61                    | 364.09                            | 287.57                         | 76.52                 | 3,771                     | 15,084                                       |
| 25                              | 137.13                    | 366.31                            | 282.01                         | 84.30                 | 3,345                     | 13,380                                       |
| 30                              | 152.61                    | 368.38                            | 276.35                         | 92.03                 | 3,003                     | 12,012                                       |
| 35                              | 168.03                    | 370.31                            | 270.60                         | 99.71                 | 2,714                     | 10,856                                       |
| 40                              | 183.38                    | 372.09                            | 264.71                         | 107.38                | 2,465                     | 9,860                                        |

The results indicated by the preceding tables are large; they vary from 9,860 to 30,580 negative calories for each kilogram of coal burned. We are far from attaining such results in practice.

We have omitted in our calculations to take into account two conditions which modify largely the theoretical results:

- 1st. The necessity of cooling the absorption chamber so that the solution of the gas may be readily accomplished.

2d. The influence of the water carried along with the gas.

We will now examine the influence of these two causes of loss.

§ 37. When ammonia gas dissolves in water, considerable heat is disengaged.

M. M. Fabre and Silbermann have measured this heat of solution, and found it equal to  $514.\text{cal}^3$  for each kilogram of gas dissolved.

The liquid of the absorption chamber being employed continually in dissolving the gas from the refrigerant, rises rapidly in temperature, and as the solubility diminishes with the temperature, it soon reaches a condition at which it ceases to work. To insure successful working it is necessary, therefore, to treat the absorption chamber to a current of cold water in such a manner as to maintain a constant temperature. We will suppose this to be the same as that of the condenser  $t_1'$ .

If we denote by  $Q_1'$  the quantity of heat, of which the absorption chamber is relieved, we shall evidently have

$$Q_1 + Q_1' = Q + Q'$$

or 
$$Q' = Q_1 + Q_1' - Q.$$

On the other hand, the gas arriving at the condenser, is always mixed with a certain quantity of steam, usually about 6 or 8 per cent. By employing a solution of calcium chloride instead of pure water for a solvent, the amount of watery vapor is reduced to about three per cent.

The presence of the steam reduces the efficiency to a notable extent. It carries off a portion of the heat of the boiler, and, having arrived in the refrigerant, it does not evaporate, but, by holding a portion of the ammonia, prevents it from volatilizing. It impedes the action then, nearly in the same way as the waste spaces in the mechanical action machines, but to a greater extent.

We will proceed to determine the influence of this introduction of water.

Let  $m$ , as before, be the weight of gas sent out from the boiler;  $\mu$  the weight of water accompanying it, and the quantities  $r$  and  $q$  affected by the index  $e$ , shall relate to the water.

When the mixture passes into the condenser, the steam becomes liquid, and absorbs a certain weight  $m'$  of gas; and we have

$$m' = \frac{0.001\beta_1'\mu}{v_1} \quad (108)$$

$\beta_1'$  being the coefficient of solubility by volume of the gas in water whose temperature is  $t_1'$ ;  $\frac{1}{v'}$  being the weight of a cubic meter of gas at this temperature.

According to Carius, the coefficient of solubility of ammonia, a gas in water, is represented by the empirical formula

$$\beta = 1049.624 - 29.4963t + 0.676873t_2 - 0.0095621t^3.$$

The quantity of heat  $Q_1$  which will be absorbed by the condenser, is equal to the quantity of heat necessary to lower the temperature of the weight  $m$  of gas from  $t_1$  to  $t_1'$ , plus the quantity of heat necessary to liquefy the weight  $m - m'$  of gas, plus the quantity of heat necessary to liquefy, and raise to the temperature  $t_1'$  the weight  $\mu$  of steam, plus the



heat disengaged by the solution of the weight  $m'$  of gas.

We shall have then

$$Q_1 = mc_p(T_1 - T_1') + (m - m')r_1' + \mu(q_{e_1} - q_{e_1}' + r_{e_1}) + m's_1', \quad (109)$$

calling  $s_1'$  the heat disengaged by the solution of one kilogram of ammonia gas in water having the temperature  $t_1'$ .

The mixture passing into the refrigerant, a certain quantity of the liquefied gas is volatilized until the pressure and temperature become equal, respectively, to  $P_2$  and  $T_2$ , the pressure and temperature of the refrigerant. The water will retain in solution a weight  $m''$  of gas, given by the equation,

$$m'' = \frac{0.001\beta_2\mu}{v_2} \quad (110)$$

The quantity of gas volatilized  $(m - m')x_2$  is found by the equation

$$\left. \begin{aligned} (m - m')x_2r_2 + (m' - m'') \\ s_2 = (m - m')(q_1 - q_2) + \\ + \mu(q_{e_1}' - q_{e_2}) + m'c_p(T_1' - T_2) \end{aligned} \right\} \quad (111)$$

The quantity of negative head realized is

$$Q = (m - m')(1 - x_2)r_2 \quad (112)$$

or

$$Q = (m - m')(r_2 - q_1' + q_2)(m' - m'') - s_2 \} - \mu(q_{e1}' - q_{e2}) - m'c_p(T_1' - T_2) \quad (113)$$

The quantity of heat  $Q_1'$  which it is necessary to supply to the absorption chamber in order to maintain a constant temperature, is equal to the heat arising from the solution of  $m - m''$  weight of gas, minus the heat necessary to raise the weight  $m$  of gas and the weight  $\mu$  of water, from  $T_2$  to  $T_1'$ .

$$Q_1' = (m - m'')s_1' - mc_p(T_1' - T_2) - \mu(q_{e1}' - q_{e2}) \quad (114)$$

The quantity of heat  $Q'$  which it is necessary to employ at the boiler, is equal to  $Q_1 + Q_1' - Q$ . We have then, applying the above values,

$$Q' = m[c_p(T_1 - T_1') + s_1'] + (m - m')[\lambda_1' - \lambda_2 - c_p(T_1' - T_2)] + (m' - m'')(s_1' - s_2) + \mu(\lambda_{1e} - q_{e1}')$$

The heat of solution  $s$  varies probably with the temperature and the pressure of

the gas, but we do not know the law of this variation, and we, therefore, assume this quantity to be constant and equal to 514.3 calories, as found by Favre and Silbermann, for ordinary temperatures and pressures.

Making  $s_1' = s_2 = s$  in the above equation it becomes

$$Q' = m[c_p(T_1 - T_1') + s] + (m - m') [\lambda_1' - \lambda_2 - c_p(T_1' - T_2)] + \mu(\lambda_{e1} - q_{e1}) \quad (115)$$

we have further

$$m = \frac{V_2}{u_2 + \frac{0.001}{\delta}} = \frac{V_2}{v_2}$$

§ 38. The two following tables exhibit results; the two cases of § 36 are taken, supposing that the weight of watery vapor carried over is 5 per cent. of the weight of the gas circulating.

First case:  $t = -15^\circ$ ,  $m = 1^k.932$ ,  $m' = 0^k.3091$ ,  $\mu = 0^k.0966$ .

| Tempera-<br>ture of<br>interior of<br>condenser<br>$t_1'$ . | Pressure<br>in<br>condenser<br>$P_1$ . | Tempera-<br>ture in<br>boiler<br>$t_1$ . | Heat carried<br>away from<br>condenser &<br>absorption<br>chamber<br>$Q_1 + Q_1'$ . | Disposa-<br>ble<br>negative<br>heat<br>$Q$ . | Heat ex-<br>pended<br>$Q'$ . | Ratio of<br>efficiency<br>theoretic<br>$\frac{Q}{Q'}$ . | Efficiency<br>per kilo-<br>gram of<br>coal<br>$\frac{Q}{4,000}$ . | Weight of<br>gas dis-<br>solved by<br>water car-<br>ried over<br>$m'$ . |
|-------------------------------------------------------------|----------------------------------------|------------------------------------------|-------------------------------------------------------------------------------------|----------------------------------------------|------------------------------|---------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------------|
| Degrees.                                                    | Kilog.                                 | Degrees.                                 | Cal.                                                                                | Cal.                                         | Cal.                         | Cal.                                                    | Cal.                                                              | Kilog.                                                                  |
| 15                                                          | 74,504                                 | 67.77                                    | 1,524.43                                                                            | 485.69                                       | 1,098.74                     | 0.442                                                   | 1,768                                                             | 0.400                                                                   |
| 20                                                          | 87,925                                 | 81.74                                    | 1,583.92                                                                            | 477.47                                       | 1,106.45                     | 0.431                                                   | 1,724                                                             | 0.407                                                                   |
| 25                                                          | 103,073                                | 95.69                                    | 1,584.80                                                                            | 470.63                                       | 1,114.17                     | 0.422                                                   | 1,688                                                             | 0.421                                                                   |
| 30                                                          | 120,083                                | 109.61                                   | 1,583.59                                                                            | 461.79                                       | 1,121.80                     | 0.411                                                   | 1,644                                                             | 0.426                                                                   |
| 35                                                          | 139,054                                | 123.47                                   | 1,577.94                                                                            | 448.70                                       | 1,129.24                     | 0.397                                                   | 1,590                                                             | 0.412                                                                   |
| 40                                                          | 160,112                                | 137.27                                   | 1,564.13                                                                            | 427.78                                       | 1,136.35                     | 0.376                                                   | 1,506                                                             | 0.364                                                                   |

Second case;  $t_2 = -30^\circ$ ,  $m = 1\text{k}.023$ ,  $m'' = 0\text{k}.147$ ,  $\mu = 0\text{k}.0511$ .

| Temperature of interior of condenser $t_1$ . | Temperature in boiler $t_1$ . | Heat carried away from condenser & absorption chamber $Q_1 + Q_1'$ . | Disposable negative heat $Q_2$ . | Heat expended $Q_3'$ . | Ratio of efficiency theoretic $\frac{Q}{Q_3'}$ . | Efficiency per kilogram of coal $\frac{4,000 Q}{Q_3'}$ . | Weight of gas dissolved by water carried over $m'$ . |
|----------------------------------------------|-------------------------------|----------------------------------------------------------------------|----------------------------------|------------------------|--------------------------------------------------|----------------------------------------------------------|------------------------------------------------------|
| Degrees.                                     | Degrees.                      | Cal.                                                                 | Cal.                             | Cal.                   | Cal.                                             | Cal.                                                     | Kilog.                                               |
| 15                                           | 106.07                        | 859.46                                                               | 258.59                           | 600.87                 | 0.430                                            | 1,721                                                    | 0.212                                                |
| 20                                           | 121.61                        | 859.88                                                               | 254.08                           | 605.80                 | 0.419                                            | 1,676                                                    | 0.215                                                |
| 25                                           | 137.13                        | 861.21                                                               | 250.57                           | 610.64                 | 0.410                                            | 1,641                                                    | 0.223                                                |
| 30                                           | 152.61                        | 861.38                                                               | 245.75                           | 615.63                 | 0.399                                            | 1,596                                                    | 0.225                                                |
| 35                                           | 168.03                        | 857.67                                                               | 238.92                           | 618.75                 | 0.386                                            | 1,544                                                    | 0.218                                                |
| 40                                           | 183.38                        | 852.93                                                               | 227.99                           | 624.94                 | 0.365                                            | 1,460                                                    | 0.193                                                |

If we compare the figures of these tables with those of § 36, we find that the cooling of the absorption chamber, and the presence of watery vapor, reduce the efficiency to a considerable extent.

We see further that the useful effect diminishes in proportion as the temperature is lowered in the refrigerant, but that the results remain the same for the same temperature of the condenser.

In the machines employing mechanical power, the efficiency on the other hand diminishes with the temperature of the refrigerant.

§ 39. In the practical manufacture of artificial ice, we estimate the performance at about 1200 or 1500 negative calories for each kilogram of coal burned, which is about 80 per cent. of the above figures. The difference here between theory and practice may fairly be attributed to external losses of temperature, to imperfect action in the exchanges of heat, and to expenditure of work in driving the pumps.

The constructors of sulphur dioxide machines claim a practical result of 2500 calories per horse power per hour. As a good engine consumes two kilograms of coal per horse power per hour, we are afforded a means of comparing the two kinds of apparatus in the matter of economy, and the result is in favor of the chemical action machines. The latter also afford the advantage of low temperatures.

In the sulphur dioxide machine, a lower temperature than  $-12^{\circ}$  is not attained without loss of useful effect, while in the ammonia machine  $-25^{\circ}$  and  $-30^{\circ}$  are readily and economically obtained.

We will not enter here upon questions of a purely practical character which affect the comparative values of the several ice machines, as our object has been simply to establish the theoretic conditions under which they work.







## APPENDIX.

NOTE UPON THE DETERMINATION OF THE  
LATENT HEAT OF VAPORIZATION, ALSO  
OF THE SPECIFIC HEAT OF SULPHUR  
DIOXIDE AND AMMONIA IN THE FORM OF  
LIQUID.

It was shown in section 27 that the relation between the pressure, specific volume and temperature of a liquefiable gas, being represented by the equation

$$Pv=BT-CP^n, \quad (116)$$

the constants B, C and  $n$  can be determined by means of the coefficient of dilatation, and the experiments of Regnault upon the compressibility of gases.

These constants are

|     | For Sulphur Dioxide. | For Ammonia. |
|-----|----------------------|--------------|
| B   | 13.882               | 52.4943      |
| C   | 3.8455               | 43.7144      |
| $n$ | 0.44487              | 0.32685      |

Regnault determined also the elastic

forces of these substances at different temperatures, and established the empirical formula

$$\log F = a + ba^t + c\beta^t.$$

This form not being convenient for calculation, we have preferred to take the formula called Roche's

$$P = a\alpha^{\frac{t}{1+mt}} \quad (117)$$

and we have calculated the three constants  $a$ ,  $\alpha$  and  $m$  for both sulphur dioxide and ammonia.

These constants are

|               | For Sulphur Dioxide.   | For Ammonia. |
|---------------|------------------------|--------------|
|               | $a=15840$ .....        | 43474.64     |
| log. $\alpha$ | $=4.1991752$ .....     | 4.6382260    |
|               | $\alpha=1.04135$ ..... | 1.0386605    |
| log. $\alpha$ | $=0.0176387$ .....     | 0.0164736    |
|               | $m=0.0043129$ .....    | 0.0040112    |

Finally M. Regnault found for the specific heat of sulphur dioxide 0.15438, and of ammonia gas 0.50836.

On the other hand Clausius established between the latent heat  $r$ , the

absolute temperature  $T$ , the pressure  $P$ , and the quantity  $u$  the relation

$$\frac{r}{u} = AT \frac{dP}{dt}$$

or

$$\frac{r}{APu} = \frac{T}{P} \frac{dP}{dt} \quad (118)$$

$u$  is the increase of volume of a unit of weight of a volatile liquid when transformed into vapor.

If  $v$  is the specific volume of the vapor, we have

$$u = v - \frac{0.001}{\delta},$$

$\delta$  being the density of the liquid, and consequently

$$APu = ABT - ACP^n \frac{0.001 \cdot AP}{\delta} \quad (119)$$

The constants  $B$ ,  $C$  and  $n$  being known, the equation will give  $APu$ .

Knowing  $APu$  we find  $r$  by eq. 118.

$$r = APu \frac{T}{P} \frac{dP}{dt}$$

or in consequence of eq. 117

$$r = APu. \frac{T.la}{(1+mt)^2} \quad (120)$$

The equation 120 will give  $r$  in terms of  $T$  and  $APu$ .

Finally it was shown in § 27 that the quantity  $\lambda$ , that is, the total heat of vaporization satisfies the equation

$$\lambda = \lambda_0 + c_p t - \frac{AC}{n} (P^n - P_0^n)$$

At temperature zero we have

$$\lambda_0 = r_0$$

then it becomes

$$\lambda = r_0 + c_p t - \frac{AC}{n} (P^n - P_0^n) \quad (121)$$

an equation in which  $P_0$  represents the pressure of the vapor at zero,  $c_p$  the specific heat of the vapor at constant pressure, and  $r_0$  the latent heat at zero.

The heat of the liquid

$$q = \lambda - r.$$

We shall have then

$$q = r_0 + c_p t - \frac{AC}{n} (P^n - P_0^n) - APu \frac{Tla}{(1+mt)} \quad (122)$$

and the specific heat of the liquid

$$c = \frac{dq}{dt}$$

The equations (119), (120), (121) and (122), involving laborious calculations, we can replace the second member by empirical expressions of the form  $A' + B't + C't^2$ , and then calculate the constants by means of three values taken at the two extremities and middle of the thermometric scale, and previously determined by aid of these equations.

We thus find for

*Sulphur Dioxide*

$$APu = 8,243 + 0,0196t - 0,000116t^2$$

$$r = 91,396 - 0,2361t - 0,000135t^2$$

$$\lambda = 91,396 + 0,12723t - 0,000131t^2$$

$$q = 0,36333t + 0,00004t^2$$

$$c = 0,36333 + 0,00008t.$$

*For Ammonia*

$$APu = 30,154 + 0,08861t - 0,000059t^2$$

$$r = 313,63 - 0,6250t - 0,002111t^2$$

$$\lambda = 313,63 + 0,3808t - 0,000282t^2$$

$$q = 1,0058t + 0,001829t^2$$

$$c = 1,0058 + 0,003658t.$$

The specific heat of liquid ammonia is nearly equal to that of water. This result, though astonishing at first, is comprehended when we reflect that the specific heat of the gas at constant pressure 0.50836 is higher than that of steam (0.4805). It would be interesting to verify by experiment the theoretical conclusion.

The results obtained here for ammonia are, however, only approximate, for we need, in order to determine the constants of eq. (116), the coefficient of dilatation of this gas, and at present it is not known.

To facilitate calculations upon the ice machines, we have prepared the following tables for sulphur dioxide and ammonia. They give for each  $5^\circ$  the heat of the liquid  $q$ , the total heat of vaporization  $\lambda$ , the latent heat of vaporization  $r$ , the internal latent heat  $\rho$ , the external latent heat  $APu$ , and the weight of a cubic meter of vapor  $\frac{1}{v}$ , for the temperatures between  $-40^\circ$  and  $+40^\circ$ .

TABLE I.—SULPHUR DIOXIDE (SATURATED).

| Temperature<br>centi-<br>grade.<br>$t$ | Absolute<br>tempera-<br>ture.<br>$T$ | Pressure in<br>kilo. per<br>meter.<br>$P$<br>(Regnault) | Total<br>heat.<br>$\lambda$ | Heat of<br>liquid.<br>$q$ | Heat of<br>vaporiz-<br>ation.<br>$r$ | Latent<br>heat<br>external.<br>$APu$ | Latent<br>heat<br>internal.<br>$\rho$ | $u$   | Weight<br>of vapor<br>per cubic<br>meter.<br>$\frac{1}{v}$ |
|----------------------------------------|--------------------------------------|---------------------------------------------------------|-----------------------------|---------------------------|--------------------------------------|--------------------------------------|---------------------------------------|-------|------------------------------------------------------------|
| -30                                    | 243                                  | 3,908                                                   | 87,461                      | -10,864                   | 98,325                               | 7,551                                | 90,774                                | 0.822 | 1,215                                                      |
| -25                                    | 348                                  | 5,082                                                   | 88,134                      | -9,058                    | 97,192                               | 7,681                                | 89,511                                | 0.641 | 1,558                                                      |
| -20                                    | 253                                  | 6,519                                                   | 88,799                      | -7,251                    | 96,050                               | 7,805                                | 88,245                                | 0.507 | 1,967                                                      |
| -15                                    | 258                                  | 8,265                                                   | 89,458                      | -5,441                    | 94,899                               | 7,923                                | 86,976                                | 0.406 | 2,456                                                      |
| -10                                    | 263                                  | 10,366                                                  | 90,111                      | -3,629                    | 93,740                               | 8,035                                | 85,705                                | 0.328 | 3,038                                                      |
| -5                                     | 268                                  | 12,874                                                  | 90,757                      | -1,814                    | 92,571                               | 8,142                                | 84,429                                | 0.268 | 3,719                                                      |
| 0                                      | 273                                  | 15,840                                                  | 91,376                      | 0,000                     | 91,396                               | 8,243                                | 83,153                                | 0.221 | 4,518                                                      |
| 5                                      | 278                                  | 19,322                                                  | 92,029                      | 1,818                     | 90,211                               | 8,338                                | 81,873                                | 0.183 | 5,447                                                      |
| 10                                     | 283                                  | 23,378                                                  | 92,655                      | 3,637                     | 89,018                               | 8,427                                | 80,591                                | 0.153 | 6,514                                                      |
| 15                                     | 288                                  | 28,074                                                  | 93,275                      | 5,459                     | 87,816                               | 8,511                                | 79,305                                | 0.129 | 7,740                                                      |
| 20                                     | 293                                  | 33,474                                                  | 93,888                      | 7,283                     | 86,605                               | 8,589                                | 78,016                                | 0.109 | 9,132                                                      |
| 25                                     | 298                                  | 39,645                                                  | 94,495                      | 9,108                     | 85,387                               | 8,661                                | 76,726                                | 0.093 | 10,718                                                     |
| 30                                     | 303                                  | 46,659                                                  | 95,095                      | 10,936                    | 84,159                               | 8,727                                | 75,432                                | 0.079 | 12,500                                                     |
| 35                                     | 308                                  | 54,585                                                  | 95,689                      | 12,765                    | 82,924                               | 8,787                                | 74,137                                | 0.068 | 14,513                                                     |
| 40                                     | —                                    | 63,496                                                  | 96,276                      | 14,597                    | 81,679                               | 8,841                                | 72,838                                | 0.057 | 16,750                                                     |

TABLE II.—AMMONIA GAS SATURATED.

| Temperature<br>centi-<br>grade.<br>$t$ | Absolute<br>tempera-<br>ture.<br>$T$ | Pressure in<br>kilo. per<br>meter.<br>$P$<br>(Regnault) | Total<br>heat.<br>$\lambda$ | Heat of<br>liquid.<br>$q$ | Heat of<br>vaporiz-<br>ation.<br>$r$ | Latent<br>heat<br>external.<br>$AP_u$ | Latent<br>heat<br>internal.<br>$\rho$ | $u$   | Weight<br>of vapor<br>per cubic<br>meter.<br>$\frac{1}{v}$ |
|----------------------------------------|--------------------------------------|---------------------------------------------------------|-----------------------------|---------------------------|--------------------------------------|---------------------------------------|---------------------------------------|-------|------------------------------------------------------------|
| -40                                    | 233                                  | 7,187                                                   | 297,967                     | -37,268                   | 335,235                              | 26,515                                | 308,720                               | 1.564 | 0.639                                                      |
| -35                                    | 238                                  | 9,302                                                   | 299,955                     | -32,963                   | 332,918                              | 26,980                                | 305,938                               | 1.230 | 0.812                                                      |
| -30                                    | 243                                  | 11,918                                                  | 301,952                     | -28,528                   | 330,480                              | 27,438                                | 303,042                               | 0.976 | 1.023                                                      |
| -25                                    | 248                                  | 15,120                                                  | 303,934                     | -23,002                   | 327,936                              | 27,902                                | 300,034                               | 0.782 | 1.276                                                      |
| -20                                    | 253                                  | 19,003                                                  | 305,901                     | -19,384                   | 325,285                              | 28,858                                | 296,927                               | 0.633 | 1.577                                                      |
| -15                                    | 258                                  | 23,669                                                  | 307,855                     | -14,676                   | 322,531                              | 28,812                                | 293,719                               | 0.516 | 1.932                                                      |
| -10                                    | 263                                  | 29,225                                                  | 309,794                     | -9,875                    | 319,669                              | 29,262                                | 290,407                               | 0.424 | 2.348                                                      |
| -5                                     | 268                                  | 35,797                                                  | 311,719                     | -4,983                    | 316,702                              | 29,708                                | 286,994                               | 0.352 | 2.840                                                      |
| 0                                      | 273                                  | 43,475                                                  | 313,630                     | 0,000                     | 313,630                              | 30,154                                | 283,476                               | 0.294 | 3.385                                                      |
| 5                                      | 278                                  | 52,405                                                  | 315,527                     | 5,075                     | 310,452                              | 30,594                                | 279,858                               | 0.247 | 4.020                                                      |
| 10                                     | 283                                  | 62,707                                                  | 317,418                     | 10,241                    | 307,177                              | 31,034                                | 276,143                               | 0.210 | 4.737                                                      |
| 15                                     | 288                                  | 74,504                                                  | 319,279                     | 15,498                    | 303,781                              | 31,470                                | 272,311                               | 0.179 | 5.543                                                      |
| 20                                     | 293                                  | 87,925                                                  | 321,133                     | 20,848                    | 300,285                              | 31,902                                | 268,383                               | 0.154 | 6.447                                                      |
| 25                                     | 298                                  | 103,073                                                 | 322,979                     | 26,288                    | 296,691                              | 32,332                                | 264,359                               | 0.133 | 7.446                                                      |
| 30                                     | 303                                  | 120,083                                                 | 324,800                     | 31,820                    | 292,980                              | 32,754                                | 260,226                               | 0.116 | 8.547                                                      |
| 35                                     | 308                                  | 139,054                                                 | 326,611                     | 37,443                    | 289,168                              | 33,182                                | 255,986                               | 0.101 | 9.766                                                      |
| 40                                     | 313                                  | 160,112                                                 | 328,431                     | 43,196                    | 285,235                              | 33,604                                | 251,631                               | 0.089 | 11.074                                                     |



